Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

S-Triggered Schmidt-type Rearrangement of Vinyl Azides to Access N-Aryl-(trifluoromethylsulfinyl)acetamides

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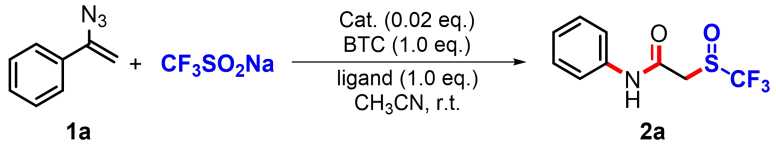
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR, ^{13}C NMR and ^{19}F spectra were recorded at 298 K on a Varian 400 MHz, 100 MHz and 376 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on Bruker Avance III HD 400M NMR Spectrometer. High resolution mass spectra (HRMS) were recorded on Bruker microTof by using ESI method.

II. Optimization of ligands

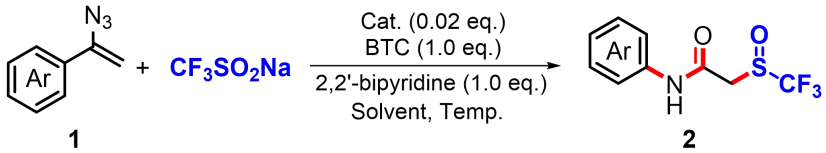


1a **2a**

Entry	Cat.	ligand	Yield/%[a]
1	$Pd(PPh_3)_4$	PPh_3	0
2	$Pd(PPh_3)_4$	Na_2CO_3	0
3	$Pd(PPh_3)_4$	1,10-phen	10
4	$Pd(PPh_3)_4$	EDTA	0
5	$Pd(PPh_3)_4$	PMDETA	0
6	$Pd(PPh_3)_4$	DBU	0
7	$Pd(PPh_3)_4$	TMEDA	0
8	$Pd(PPh_3)_4$	pyridine	15
9	$Pd(PPh_3)_4$	DMAP	trace
10	$Pd(PPh_3)_4$	4,4'-bipyridine	20

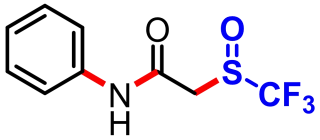
[a]Conditions: **1a** (0.5 mmol), CF_3SO_2Na (0.75 mmol), BTC (0.5 mmol), ligand (0.5 mmol), $Pd(PPh_3)_4$ (0.01 mmol), CH_3CN (2 mL) at r.t. under Ar for 3 h; Yields of isolated products. EDTA = ethylenediaminetetraacetic acid; PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine; DMAP = 4-dimethylaminopyridine; DBU=1,8-diazabicyclo[5,4,0]undec-7-ene; TMEDA = N,N,N',N'-tetramethylethylenediamine.

II. Synthesis and analytical data of compounds 2

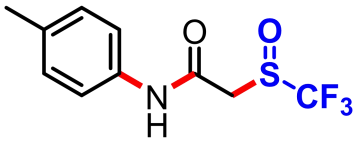


1 2

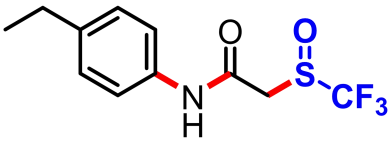
Genernal procedure: Under argon atmosphere, sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), triphosgene (BTC) (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.) were added in an oven-dried 15 mL Schlenk tube with 1 mL CH_3CN, then vinyl azide **1** (78.0 μL, 0.5 mmol, 1.0 eq.) in 1 mL CH_3CN was added in the above mixed solution. The reaction mixture was then stirred for 3 h at room temperature when TLC conformed that substrate **1** had been consumed. The reaction was followed by adding 30 mL H_2O and taken up with dichloromethane (3×15 mL). The combined organic layer was washed with brine (3×40 mL), dried over $MgSO_4$ and concentrated under reduced pressure.The residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate) and the target product was afforded.



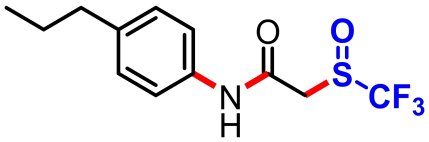
(2a) 0.5 mmol scale: Prepared following the genernal procedure showed above using (1-azidovinyl)benzene (72.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (103.0 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.53-7.47 (m, 2H), 7.38-7.30 (m, 2H), 7.22-7.13 (m, 1H), 3.94 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 136.7, 129.2, 125.5, 125.1 (q, J = 334.8 Hz), 120.4, 53.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.96; **HRMS** (ESI-TOF) m/z calculated for $C_9H_8F_3NO_2SNa$ $[M+Na]^+$: 274.0126, found: 274.0135.



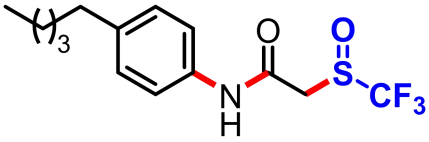
(2b) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-methylbenzene (79.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethyl sulfonate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (116.7 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.39-7.33 (m, 2H), 7.15-7.08 (m, 2H), 3.99-3.88 (m, 2H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 135.2, 134.2, 129.6, 125.1 (q, J = 333.8 Hz), 120.4, 53.4, 20.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.06 ; **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{10}F_3NO_2SNa$ $[M+Na]^+$: 288.0282, found: 288.0289.



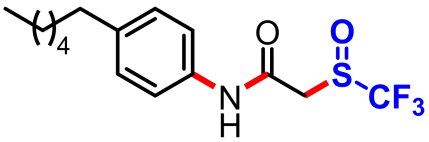
(2c) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-ethylbenzene (86.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (117.3 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.43-7.35 (m, 2H), 7.18-7.12 (m, 2H), 3.99-3.88 (m, 2H), 2.66-2.55 (m, 2H), 1.21 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 141.7, 134.3, 128.5, 125.1 (q, J = 328.5 Hz), 120.5, 53.7, 28.4, 15.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.04; **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{12}F_3NO_2SNa$ $[M+Na]^+$: 302.0439, found: 302.0432.



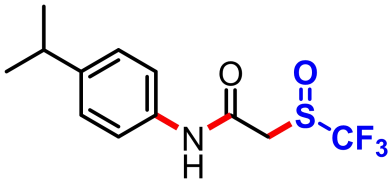
(2d) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-propylbenzene (93.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (126.1 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.42-7.36 (m, 2H), 7.17-7.11 (m, 2H), 3.98-3.88 (m, 2H), 2.61-2.51 (m, 2H), 1.66-1.59 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 140.1, 134.3, 129.1, 125.1 (q, *J* = 325.6 Hz), 120.4, 53.6, 37.5, 24.5, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.08; **HRMS** (ESI-TOF) m/z calculated for $C_{12}H_{14}F_3NO_2SNa$ $[M+Na]^+$: 316.0595, found: 316.0592.



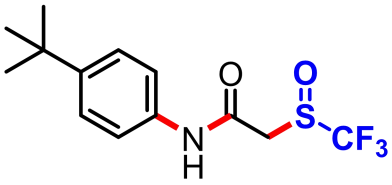
(2e) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-pentylbenzene (107.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (121.9 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.38-7.34 (m, 2H), 7.12-7.07 (m, 2H), 4.04-3.87 (m, 2H), 2.64-2.48 (m, 2H), 1.65-1.52 (m, 2H), 1.35-1.27 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 140.3, 134.3, 129.0, 125.2 (q, *J* = 338.1 Hz), 120.4, 54.2, 35.4, 31.4, 31.1, 22.5, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.12; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{18}F_3NO_2SNa$ $[M+Na]^+$: 344.0908, found: 344.0912.



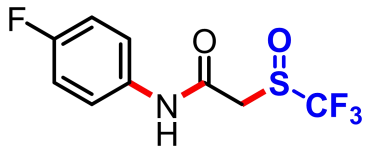
(2f) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-hexylbenzene (114.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (130.7 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.37-7.30 (m, 2H), 7.12-7.04 (m, 2H), 4.07-3.87 (m, 2H), 2.64-2.48 (m, 2H), 1.62-1.51 (m, 2H), 1.34-1.24 (m, 6H), 0.95-0.85 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 140.3, 134.3, 128.9, 125.2 (q, J = 329.7 Hz), 120.4, 54.4, 35.4, 31.7, 31.4, 28.9, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.22; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{20}F_3NO_2SNa$ $[M+Na]^+$: 358.1065, found: 358.1067.



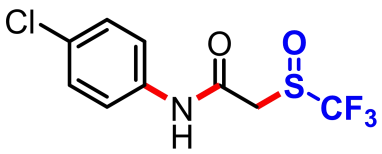
(2g) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-iso-propyl phenylenyl azide (93.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (123.2 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.41-7.35 (m, 2H), 7.20-7.15 (m, 2H), 4.02-3.88 (m, 2H), 2.93-2.82 (m, 1H), 1.22 (d, J = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 146.2, 134.4, 127.0, 125.1 (q, J = 335.8 Hz), 120.5, 53.9, 33.6, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.11; **HRMS** (ESI-TOF) m/z calculated for $C_{12}H_{14}F_3NO_2SNa$ $[M+Na]^+$: 316.0595, found: 316.0605.



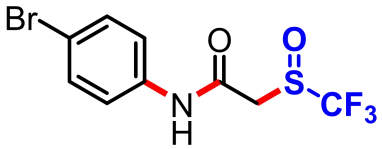
(2h) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-(tert-butyl)benzene (100.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (124.5 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.42-7.36 (m, 2H), 7.35-7.30 (m, 2H), 4.03-3.87 (m, 2H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 148.5, 134.1, 125.9, 125.1 (q, J = 333.5 Hz), 120.2, 54.3, 34.5, 31.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.09; **HRMS** (ESI-TOF) m/z calculated for $C_{13}H_{16}F_3NO_2SNa$ $[M+Na]^+$: 330.0752, found: 330.0756.



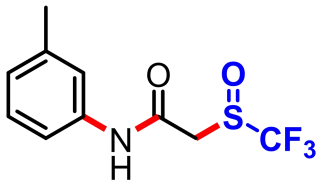
(2i) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-fluorobenzene (81.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (98.3 mg, 73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.49-7.38 (m, 2H), 7.03-6.95 (m, 2H), 4.03-3.88 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 159.3 (d, J = 247.7 Hz), 133.9, 125.5 (q, J = 334.6 Hz), 121.6 (d, J = 8.9 Hz), 115.4 (d, J = 22.3 Hz), 56.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.89, -116.18; **HRMS** (ESI-TOF) m/z calculated for $C_9H_7F_4NO_2SNa$ $[M+Na]^+$: 292.0031, found: 292.0006.



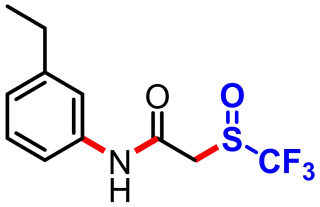
(2j) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-chlorobenzene (89.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (112.8 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.43-7.37 (m, 2H), 7.28-7.22 (m, 2H), 4.10-3.80 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 135.3, 130.5, 129.1, 125.0 (q, J = 326.1 Hz), 121.4, 53.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.86; **HRMS** (ESI-TOF) m/z calculated for $C_9H_7ClF_3NO_2SNa$ $[M+Na]^+$: 307.9736, found: 307.9713.



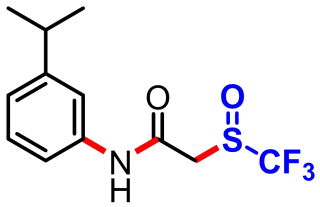
(2k) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-4-bromobenzene (111.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (125.4 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.45-7.35 (m, 4H), 4.01-3.88 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 135.8, 132.1, 125.0 (q, J = 334.8 Hz), 121.8, 118.2, 53.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.81; **HRMS** (ESI-TOF) m/z calculated for $C_9H_7BrF_3NO_2SNa$ $[M+Na]^+$: 351.9231, found: 351.9209.



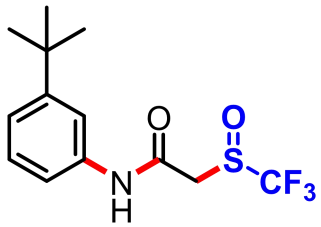
(2l) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3-methylbenzene (79.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (108.8 mg, 82%);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.35-7.24 (m, 2H), 7.22-7.15 (m, 1H), 7.00-6.93 (m, 1H), 4.02-3.88 (m, 2H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 139.1, 136.6, 128.9, 126.3, 125.0 (q, J = 331.0 Hz), 121.0, 117.4, 54.0, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.02; **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{10}F_3NO_2SNa$ $[M+Na]^+$: 288.0282, found: 288.0279.



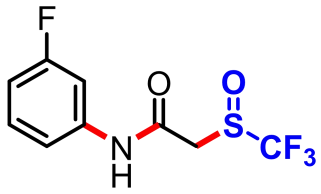
(2m) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3-ethylbenzene (86.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (115.9 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.36-7.30 (m, 2H), 7.27-7.21 (m, 1H), 7.04-6.98 (m, 1H), 3.93 (s, 2H), 2.69-2.58 (m, 2H), 1.23 (t, J = 7.6 Hz, 3H)； **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 145.6, 136.7, 129.1, 125.2 (q, J = 339,1 Hz), 125.1, 119.9, 117.8, 53.4, 28.8, 15.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.05; **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{12}F_3NO_2SNa$ $[M+Na]^+$: 302.0439, found: 302.0427.



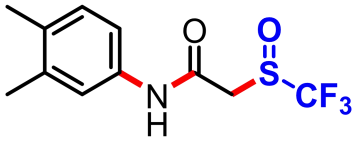
(2n) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3-isopropylbenzene (93.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (118.8 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.37-7.31 (m, 2H), 7.26-7.20 (m, 1H), 7.06-6.99 (m, 1H), 4.01-3.88 (m, 2H), 2.93-2.82 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 150.2, 136.7, 129.1, 125.1 (q, *J* = 333.6 Hz), 123.6, 118.5, 117.9, 53.8, 34.1, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.12; **HRMS** (ESI-TOF) m/z calculated for $C_{12}H_{14}F_3NO_2SNa$ $[M+Na]^+$: 316.0595, found: 316.0604.



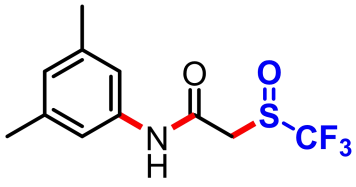
(2o) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3-(tert-butyl)benzene (100.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (122.9 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.45-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.30-7.22 (m, 1H), 7.21-7.17 (m, 1H), 4.01-3.88 (m, 2H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 152.5, 136.5, 128.8, 125.2 (q, *J* = 330.6 Hz), 122.6, 117.7, 117.5, 53.8, 34.8, 31.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.13; **HRMS** (ESI-TOF) m/z calculated for $C_{13}H_{16}F_3NO_2SNa$ $[M+Na]^+$: 330.0752, found: 330.0747.



(2p) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3-fluorobenzene (81.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (114.4 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.45-7.35 (m, 1H), 7.26-7.17 (m, 1H), 7.12-7.05 (m, 1H), 6.88-6.79 (m, 1H), 4.08-3.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, J = 241.9 Hz), 160.9, 139.3 (d, J = 11.4 Hz), 130.1 (d, J = 18.8 Hz), 125.1 (q, J = 339.7 Hz), 115.3, 111.4 (d, J = 19.5 Hz), 107.4 (d, J = 23.1 Hz), 56.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.79, -110.86; **HRMS** (ESI-TOF) m/z calculated for $C_9H_7F_4NO_2SNa$ $[M+Na]^+$: 292.0031, found: 292.0009.



(2q) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-(1-azidovinyl)-1,2-dimethylbenzene (86.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (113.1 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.26-7.19 (m, 2H), 7.11-7.05 (m, 1H), 3.98-3.86 (m, 2H), 2.23 (d, J = 5.2 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 137.5, 134.4, 134.0, 130.1, 125.1 (q, J = 327.8 Hz), 121.7, 118.0, 53.6, 19.8, 19.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.13; **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{12}F_3NO_2SNa$ $[M+Na]^+$: 302.0439, found: 302.0426.



(2r) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-(1-azidovinyl)-3,5-dimethylbenzene (86.5 mg, 0.5 mmol, 1.0 eq.), sodium trifluoromethanesulfinate (117.0 mg, 0.75 mmol, 1.5 eq.), BTC (148.4 mg, 0.5 mmol, 1.0 eq.), 2,2'-bipyridine (78.1 mg, 0.5 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 0.02 eq.), The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (114.5 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.13 (s, 2H), 6.81 (s, 1H), 3.91 (s, 2H), 2.30 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 143.2, 142.4, 131.1, 127.0 (q, J = 363.7 Hz), 122.4, 61.1, 26.1, 23.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.00; **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{12}F_3NO_2SNa$ $[M+Na]^+$: 302.0439, found: 302.0423.

IV. Crystallography of compound 2b

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.1 Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. 1 (a) G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Gottingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

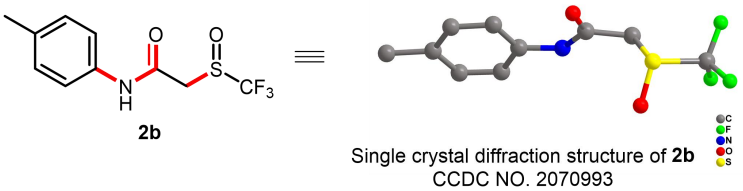
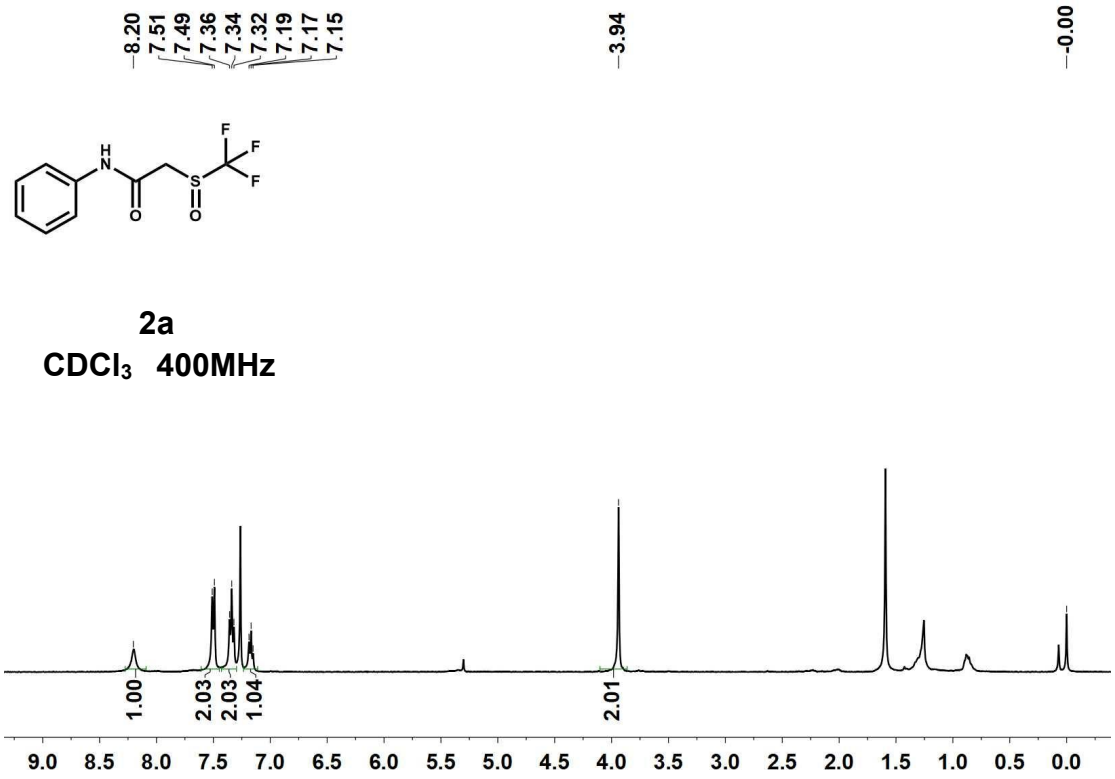


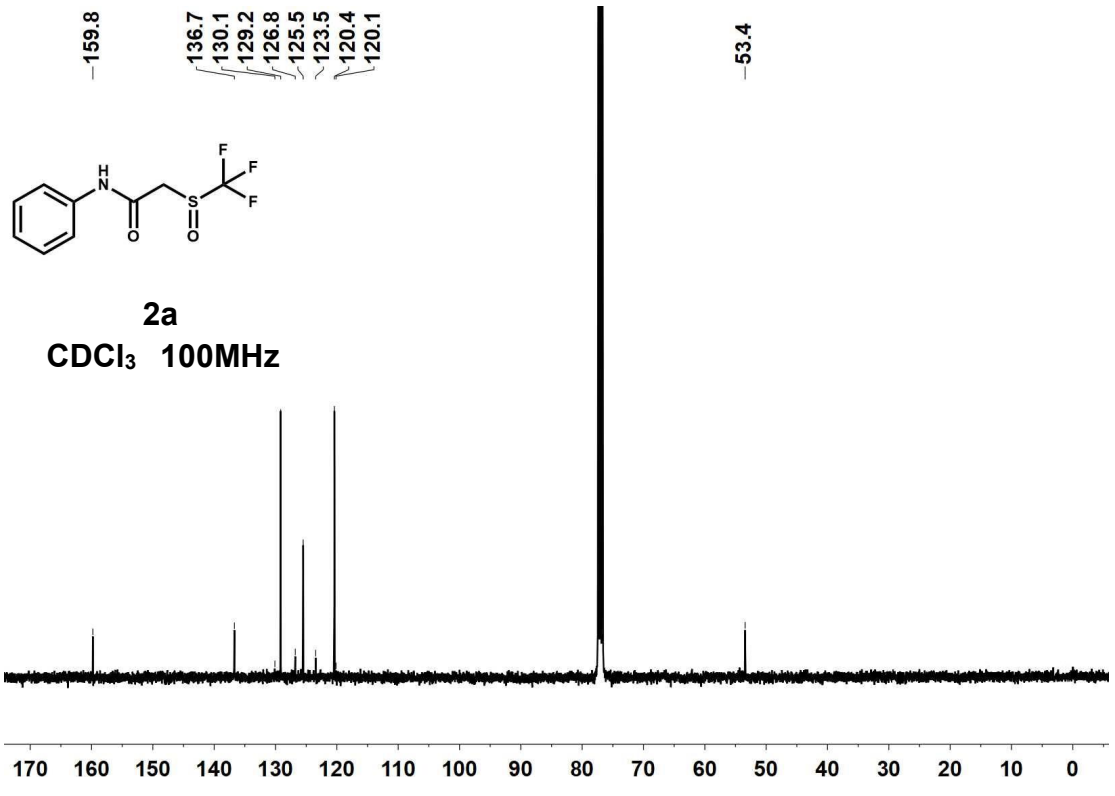
Table 1. Crystal data and structure refinement.

Empirical formula	$C_{10}H_{10}F_3NO_2S$
Temperature	293(2) K
Wavelength	1.54178 Å
Unit cell dimensions	a = 13.1954(9) Å alpha = 90.00 ° b = 10.2798(9) Å beta = 96.658(7) ° c = 8.7100(8) Å gamma = 90.00 °
Volume	1173.51(17) $Å^3$
Z	4
Calculated density	1.501 mg/mm^3
Absorption coefficient	0.304 mm^{-1}
F(000)	544.0
Crystal size	0.24 × 0.15 × 0.07 mm^3
Theta range for data collection	6.64 to 58.52°
Reflections collected /Independent reflections	7805 /2740 [R_{int} = 0.0276, R_{sigma} = 0.0329]
Data / restraints / parameters	2740 / 0 / 155
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R_1 = 0.0468, wR_2 = 0.1177
Final R indices (all data)	R_1 = 0.0647, wR_2 = 0.1349

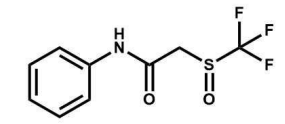
IV. NMR spectra copies



2a
$CDCl_3$ 400MHz

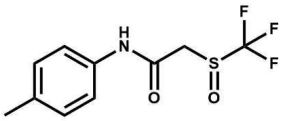


2a
$CDCl_3$ 100MHz



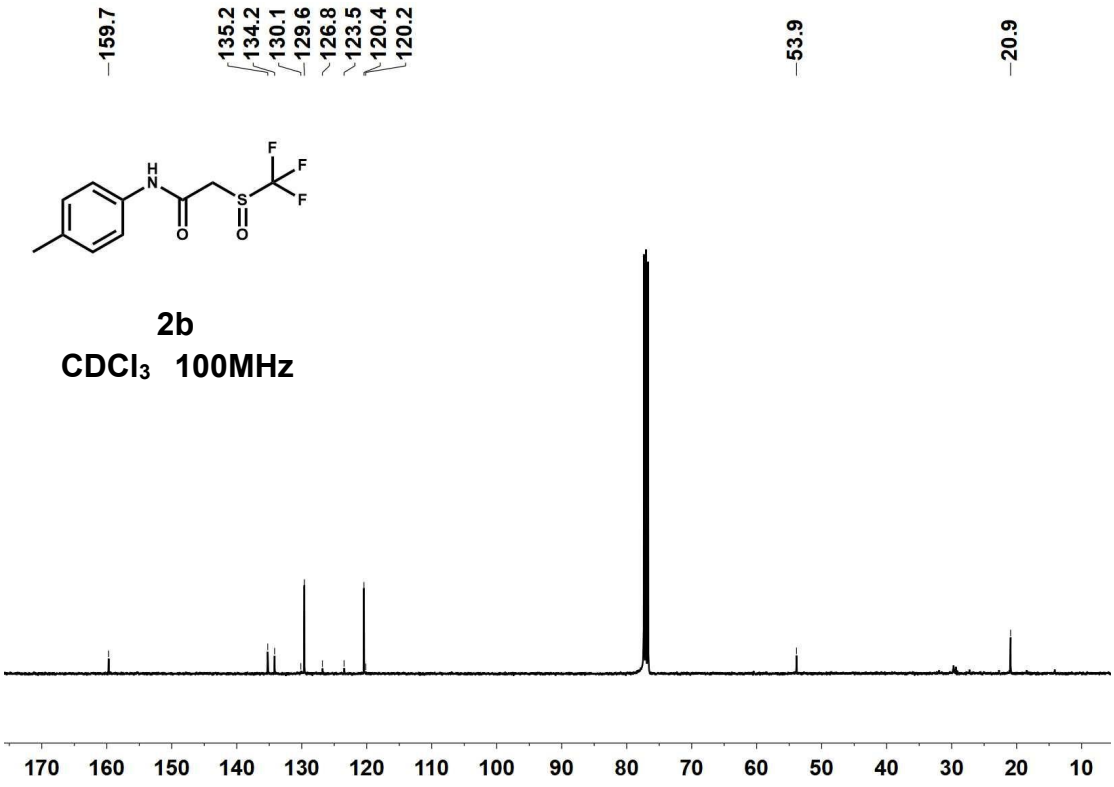
2a

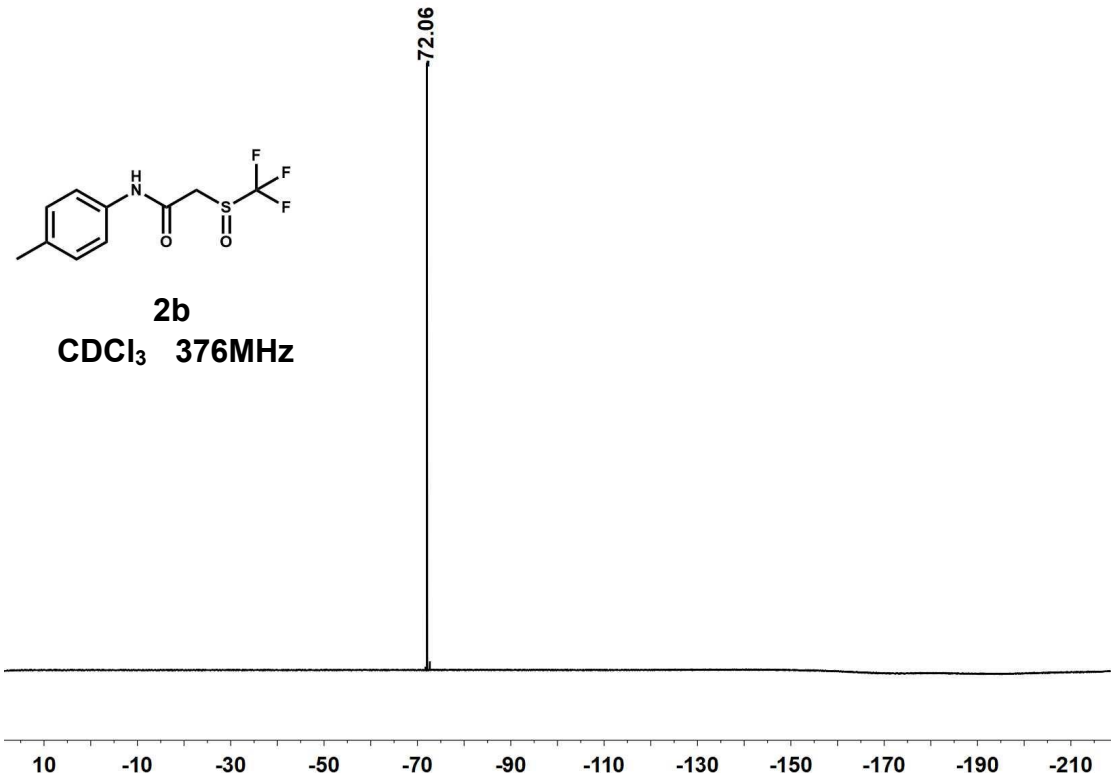
$CDCl_3$ 376MHz

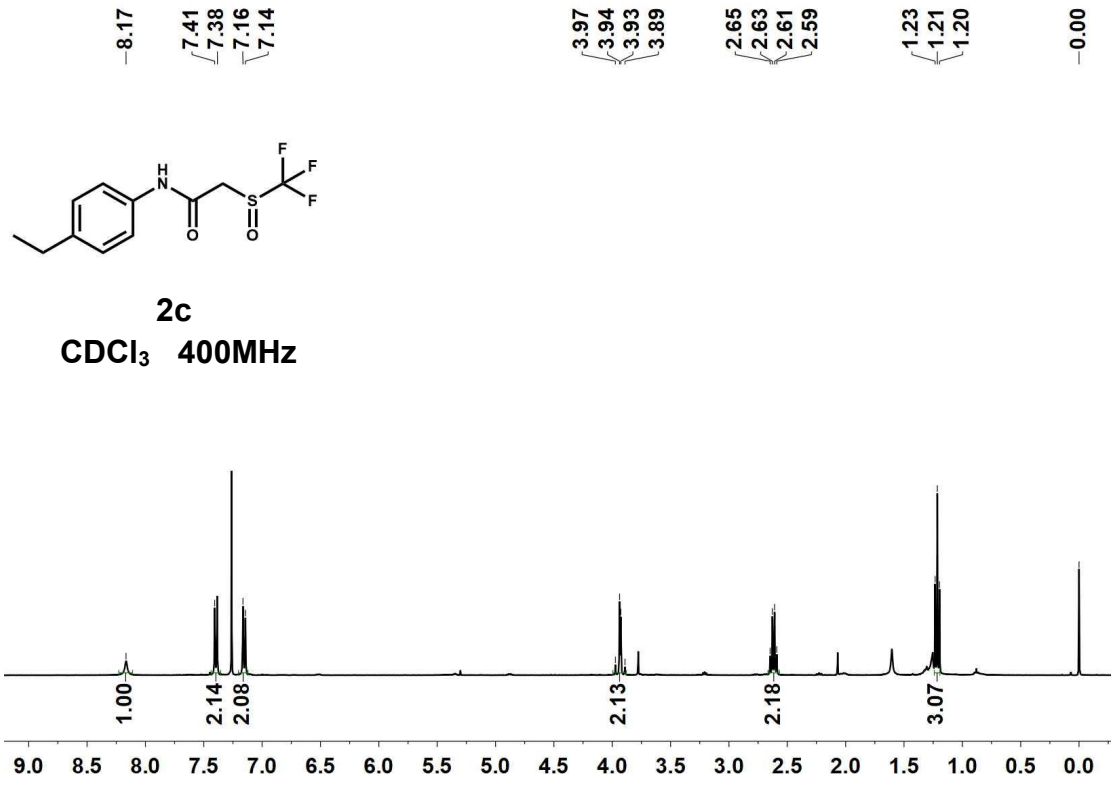


2b

$CDCl_3$ 400MHz


159.7
135.2
134.2
130.1
129.6
126.8
123.5
120.4
120.2
53.9
20.9
2b
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


72.06
2b
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



2c

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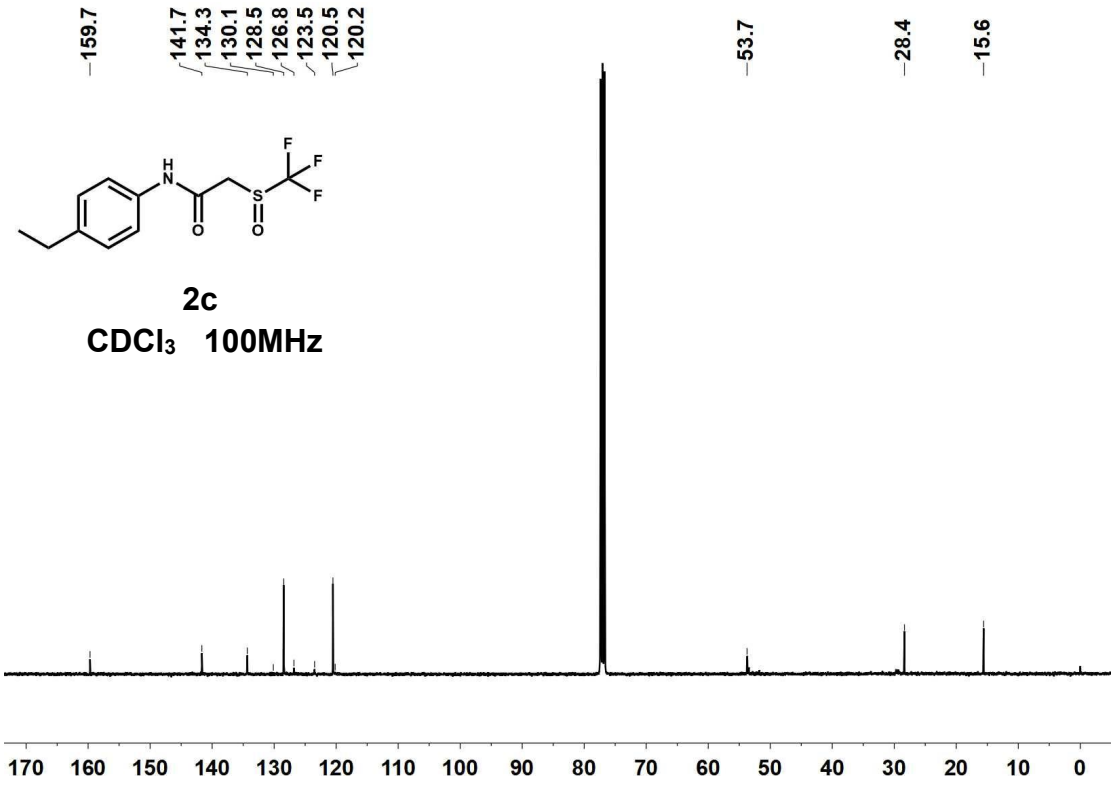
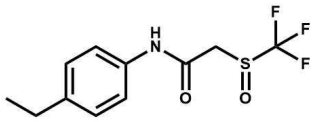


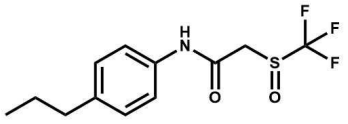
2c

$CDCl_3$ 100MHz



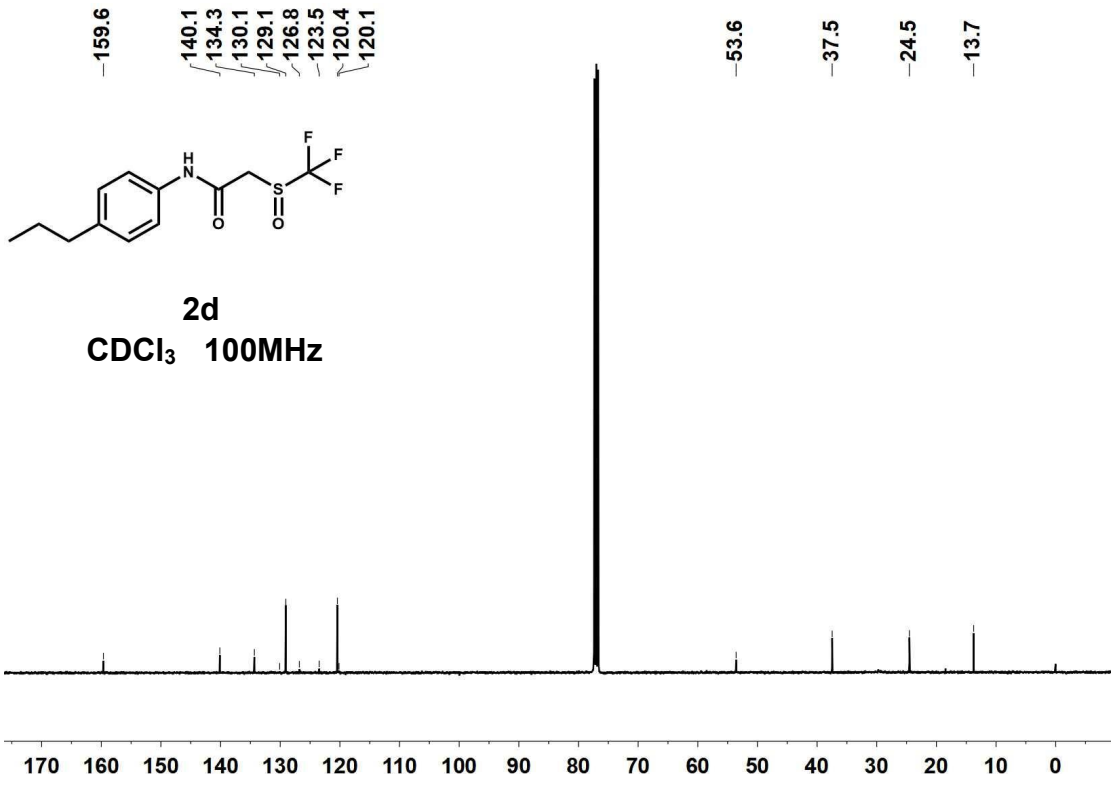
2c

$CDCl_3$ 376MHz



2d

$CDCl_3$ 400MHz


159.6
140.1
134.3
130.1
129.1
126.8
123.5
120.4
120.1
53.6
37.5
24.5
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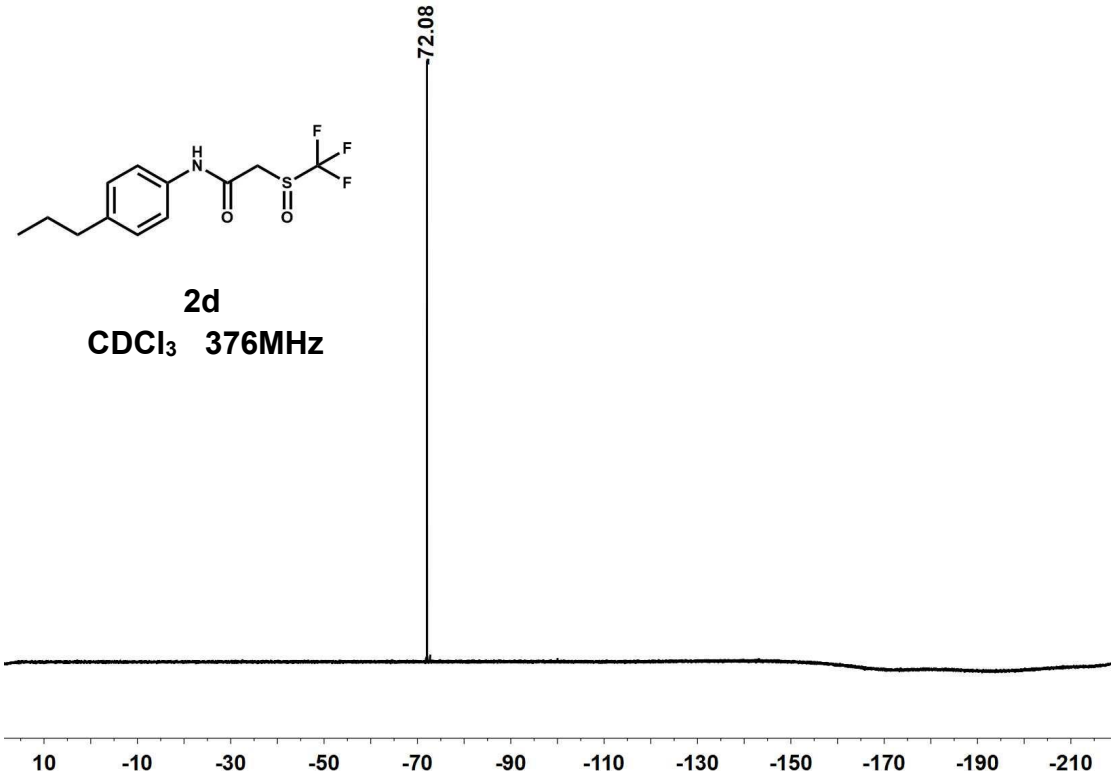
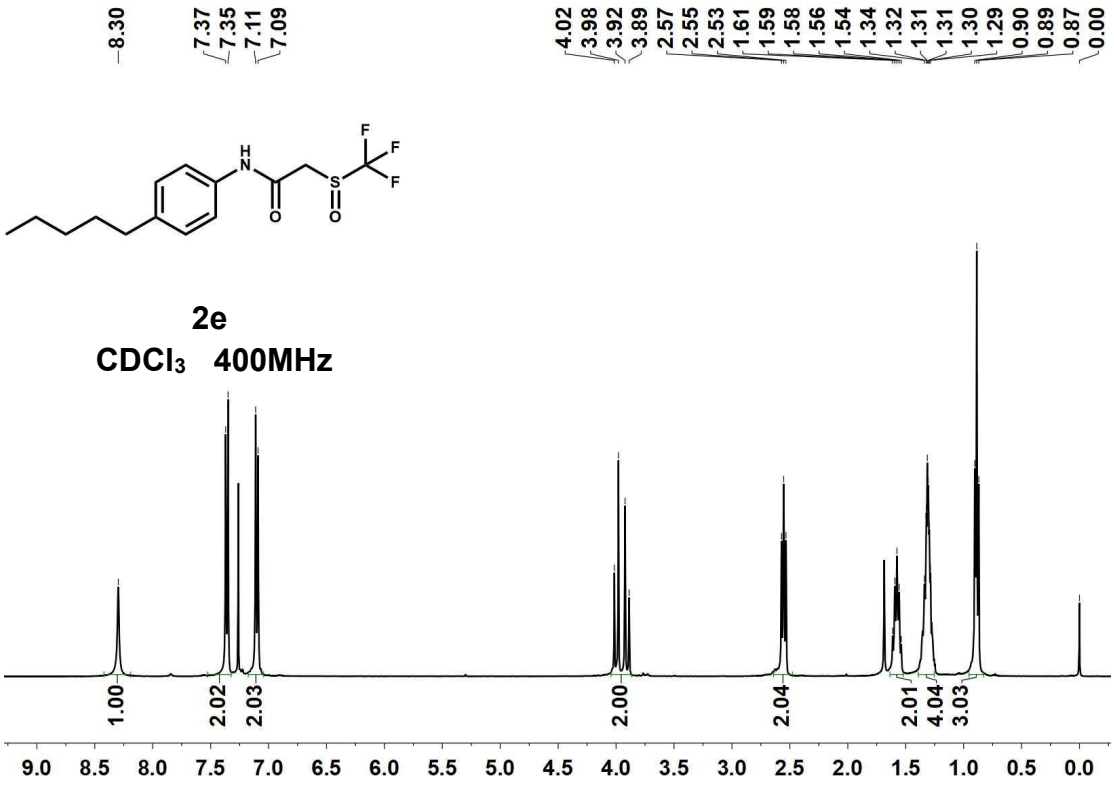
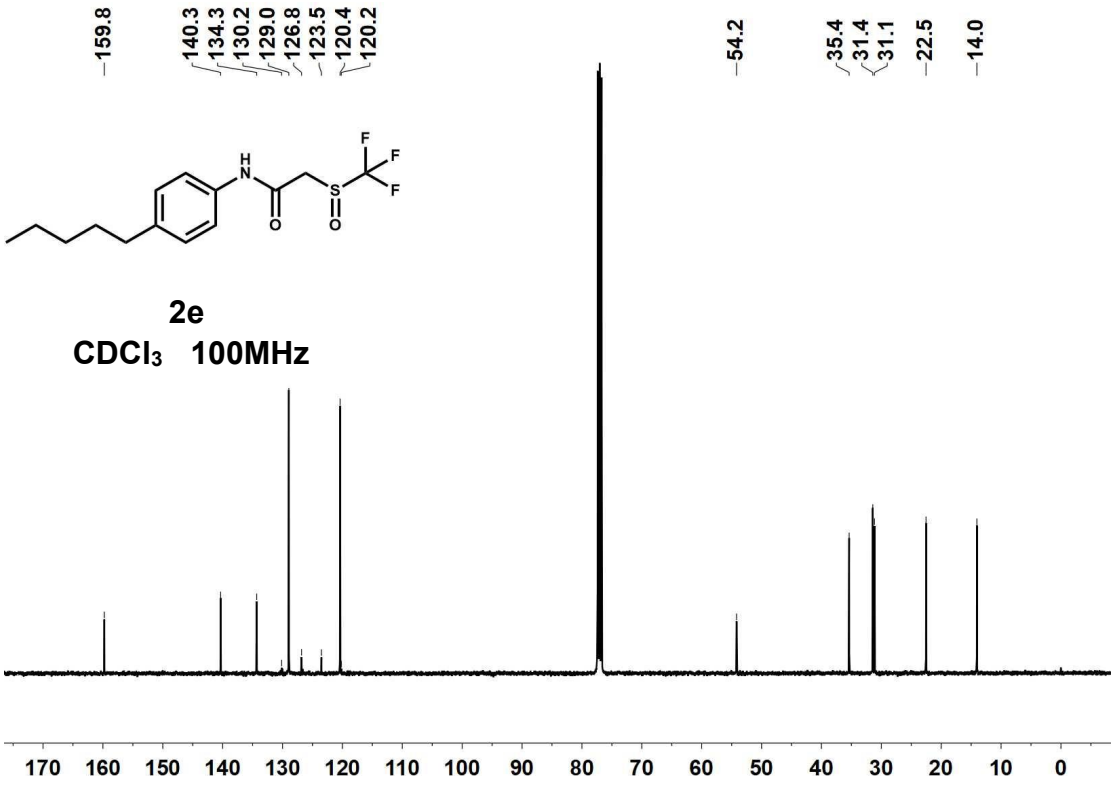
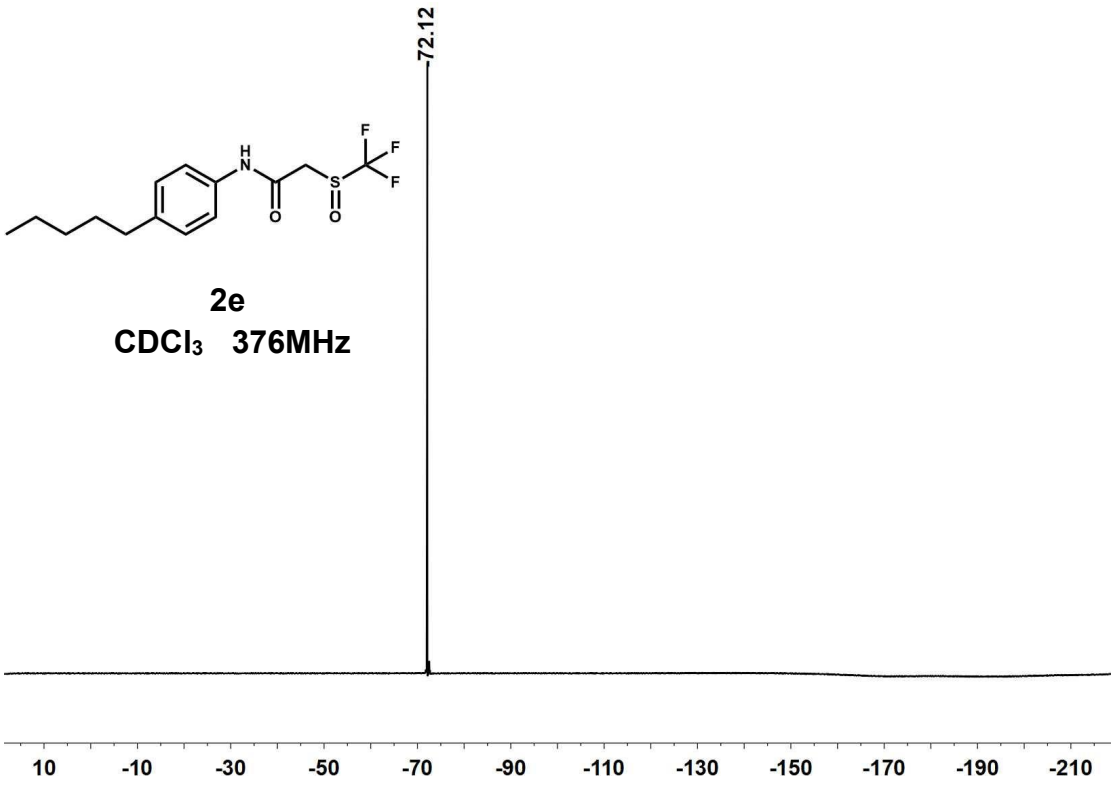
2d
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


72.08
2d
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

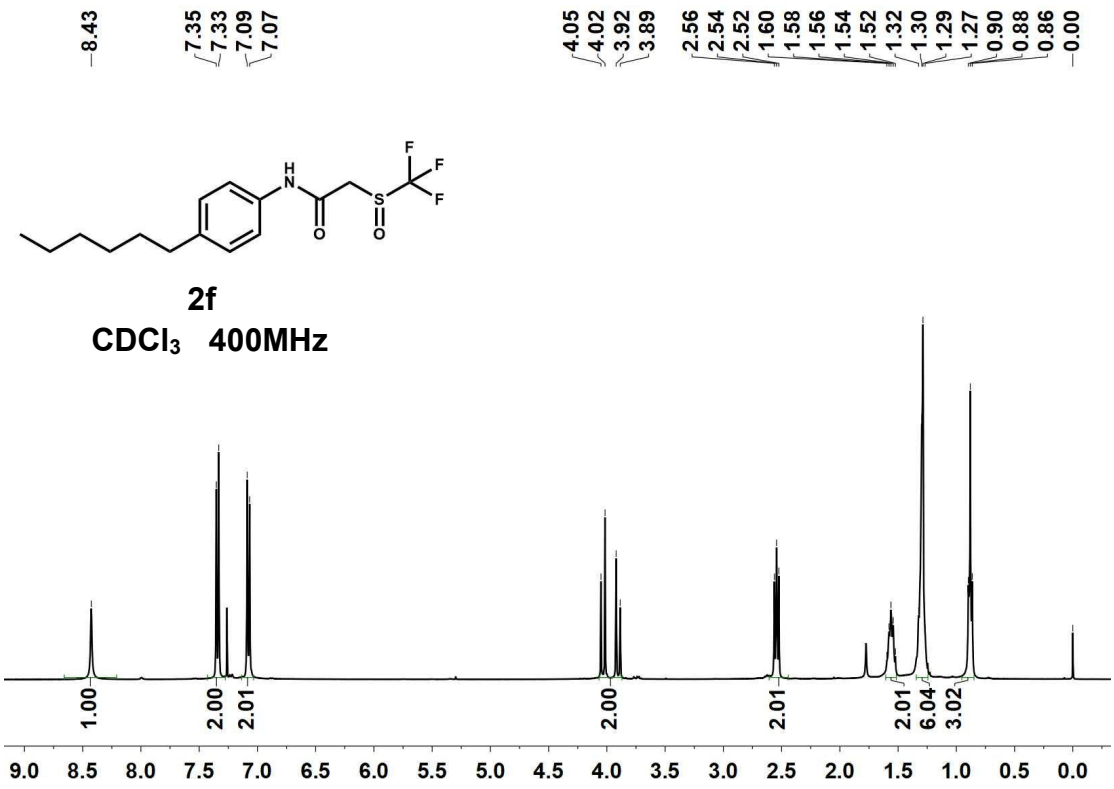

8.30
7.37
7.35
7.11
7.09
4.02
3.98
3.92
3.89
2.57
2.55
2.53
1.61
1.59
1.58
1.56
1.54
1.34
1.32
1.31
1.31
1.30
1.29
0.90
0.89
0.87
0.00
2e
CDCl3 400MHz
1.00
2.02
2.03
2.00
2.04
2.01
4.04
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


159.8
140.3
134.3
130.2
129.0
126.8
123.5
120.4
120.2
54.2
35.4
31.4
31.1
22.5
14.0
2e
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



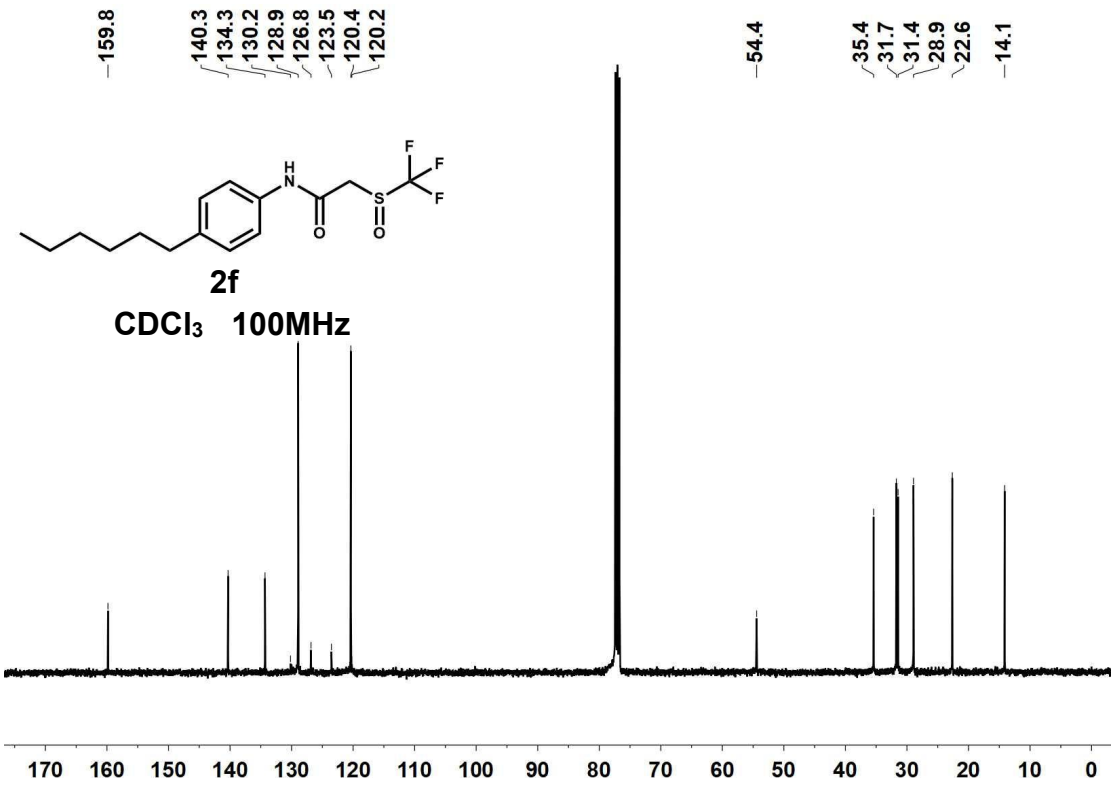
2e

$CDCl_3$ 376MHz



2f

$CDCl_3$ 400MHz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140.3
134.3
130.2
128.9
126.8
123.5
120.4
120.2
54.4
35.4
31.7
31.4
28.9
22.6
14.1
2f
CDCl3 100MHz
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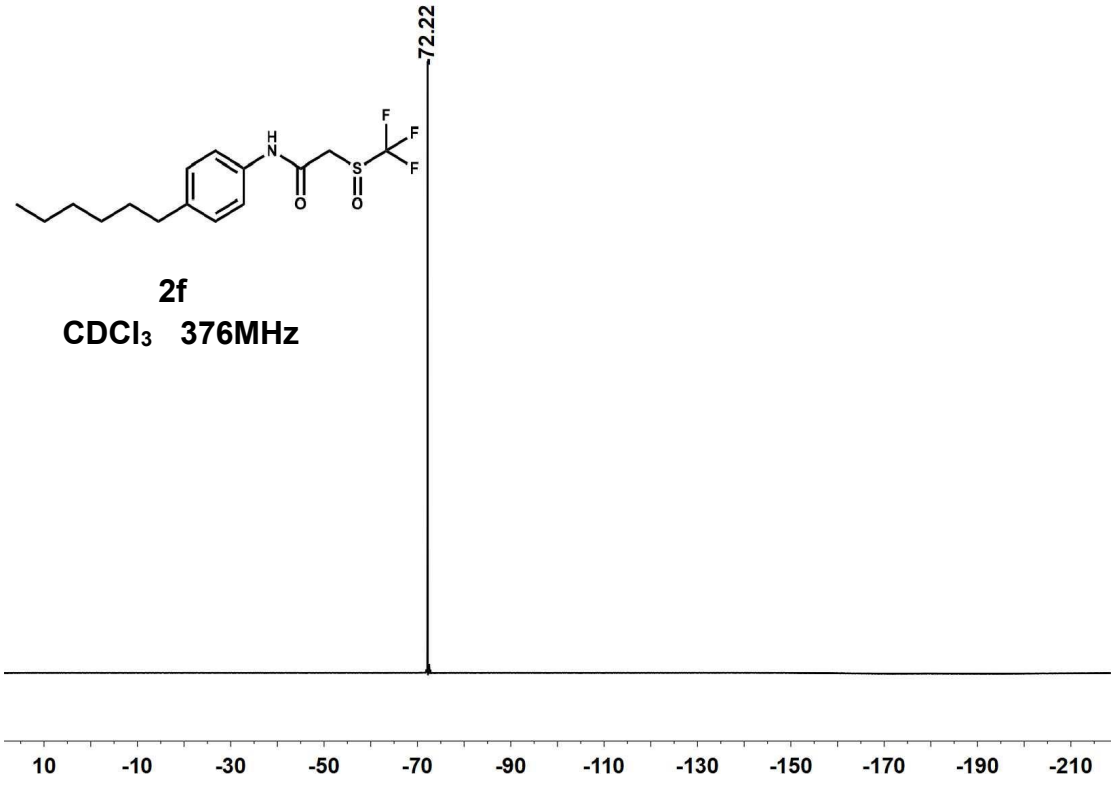
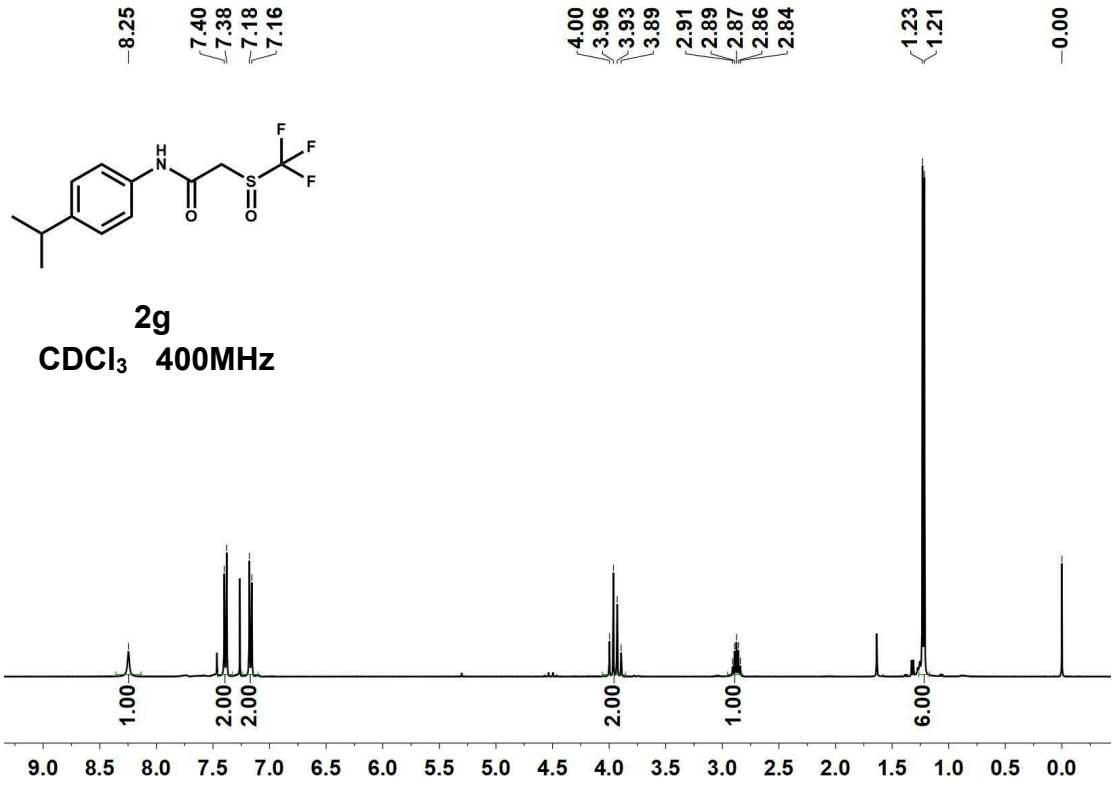
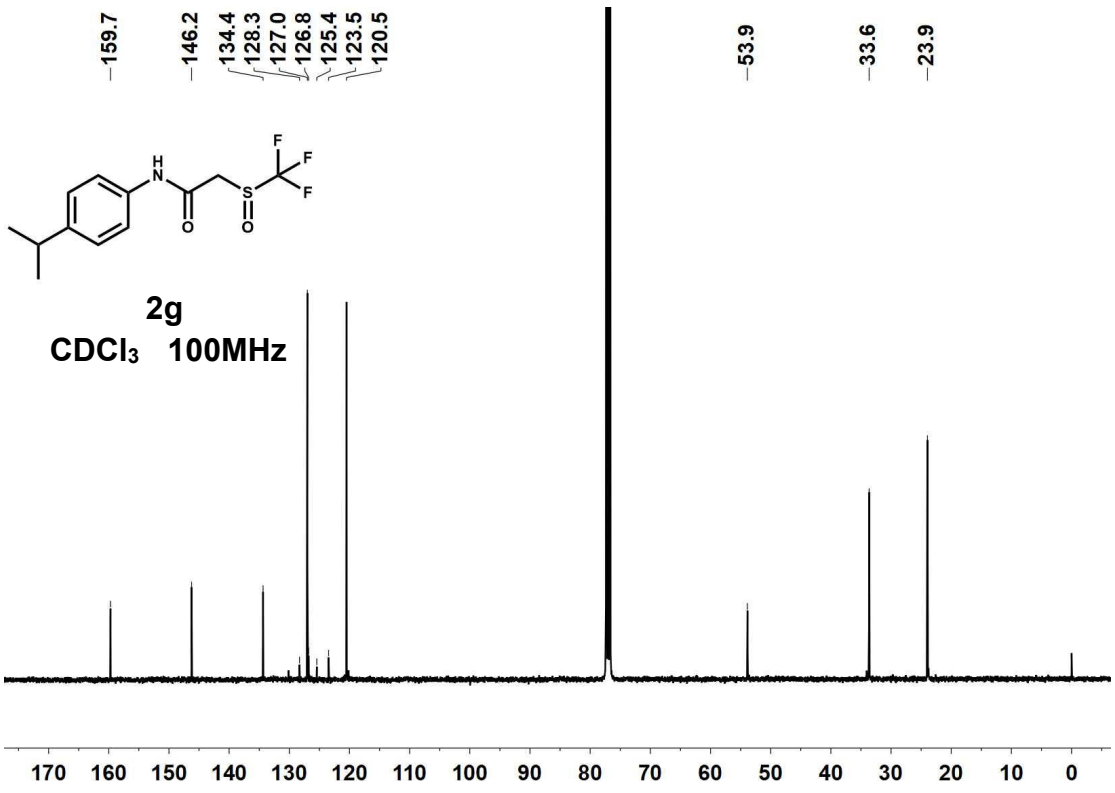

72.22
2f
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



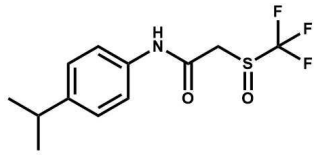
2g

$CDCl_3$ 400MHz



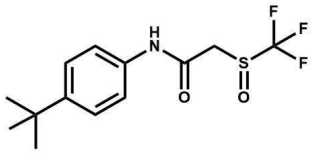
2g

$CDCl_3$ 100MHz



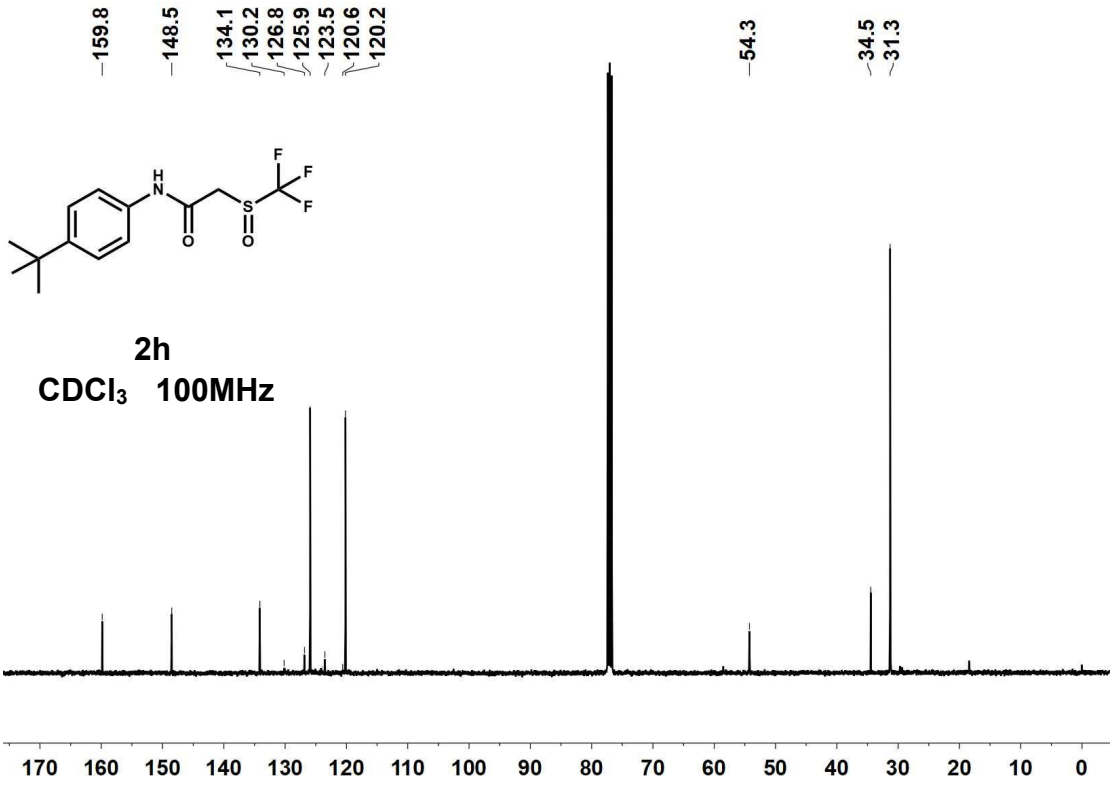
2g

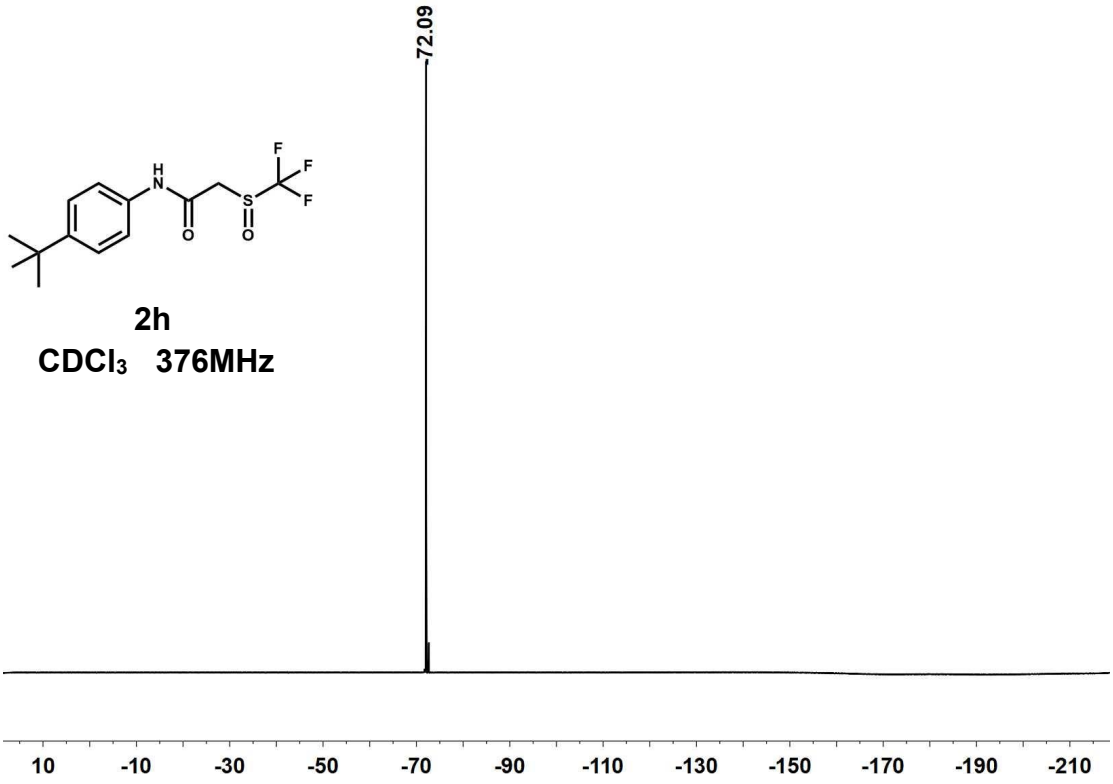
$CDCl_3$ 376MHz

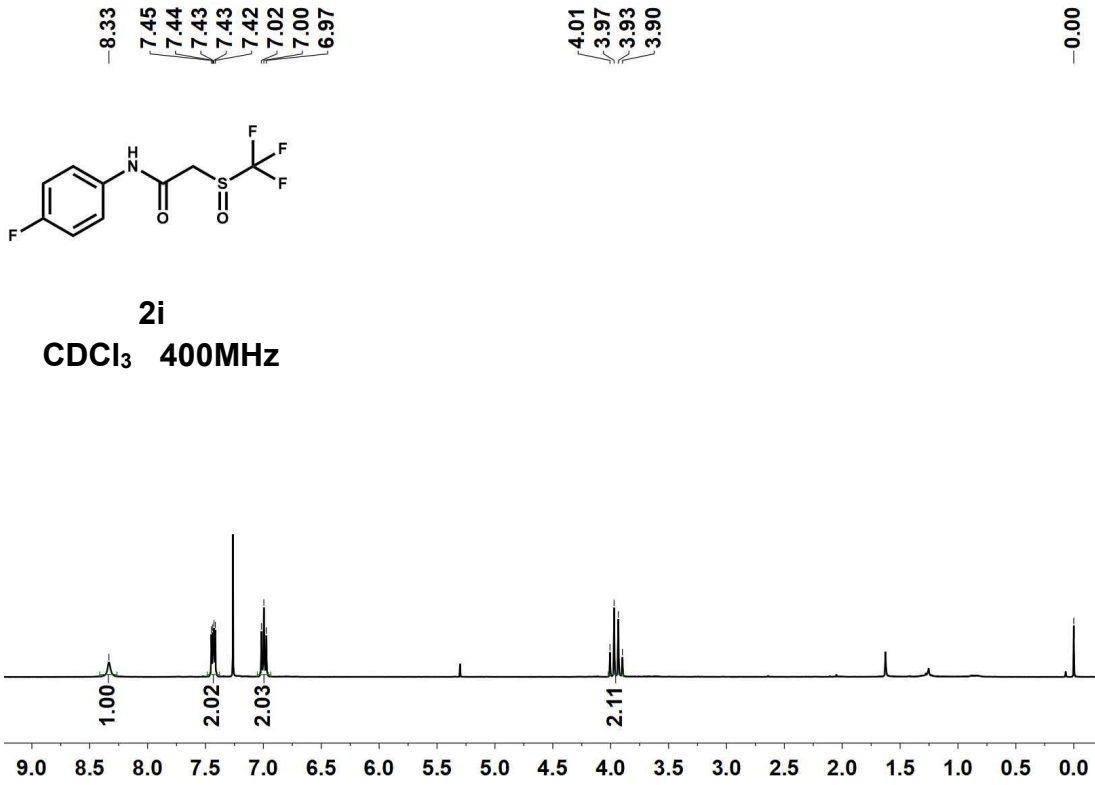


2h

$CDCl_3$ 400MHz

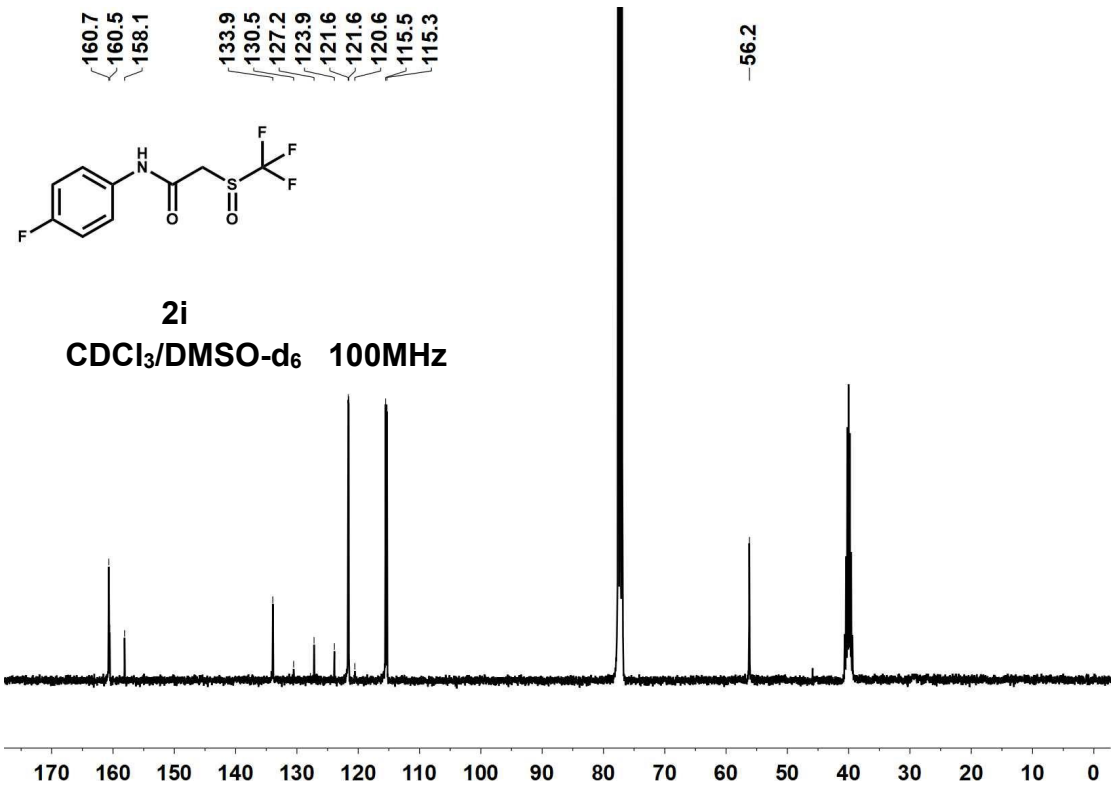

159.8
148.5
134.1
130.2
126.8
125.9
123.5
120.6
120.2
54.3
34.5
31.3
2h
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


72.09
2h
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



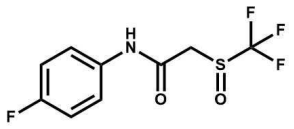
2i

$CDCl_3$ 400MHz

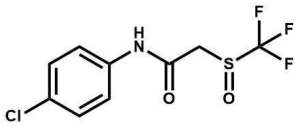


2i

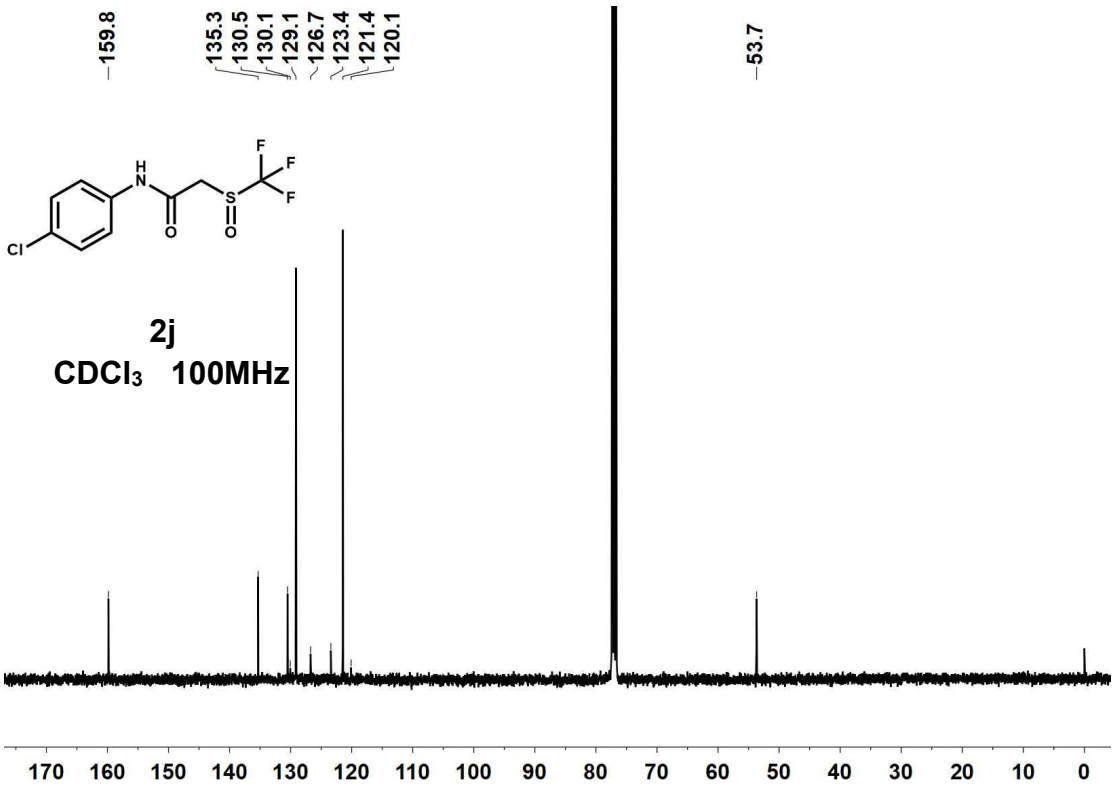
$CDCl_3$/DMSO-d_6 100MHz

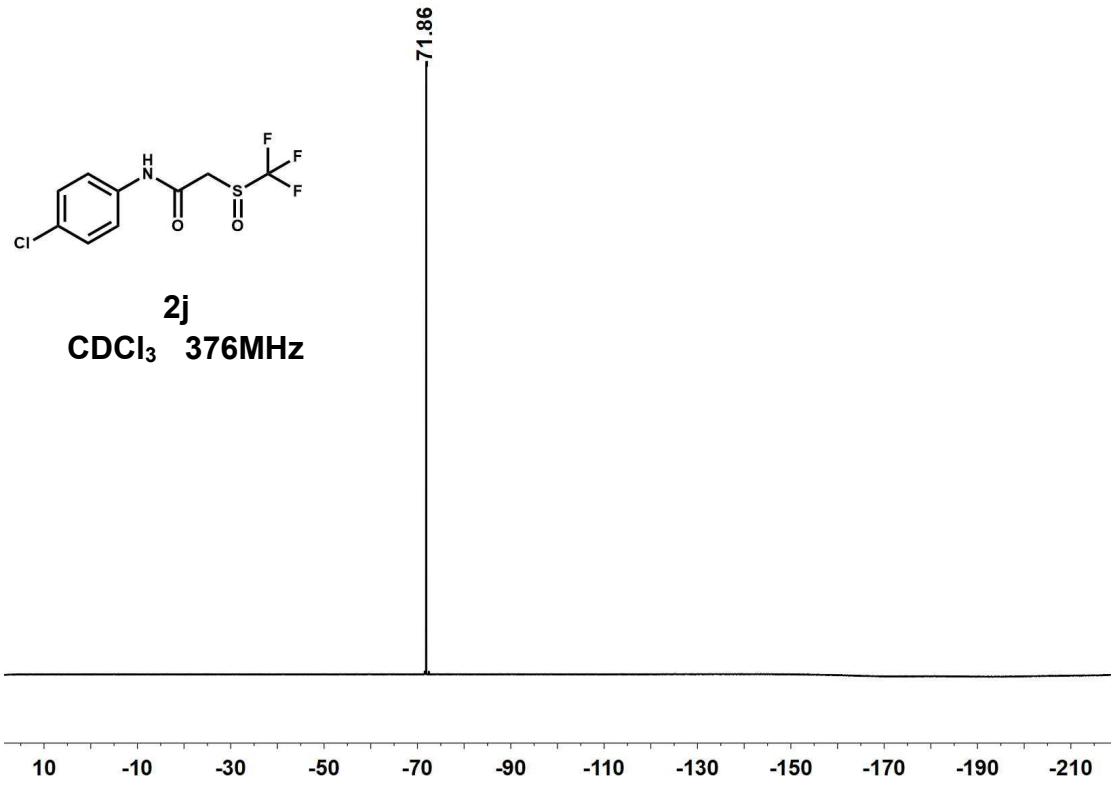


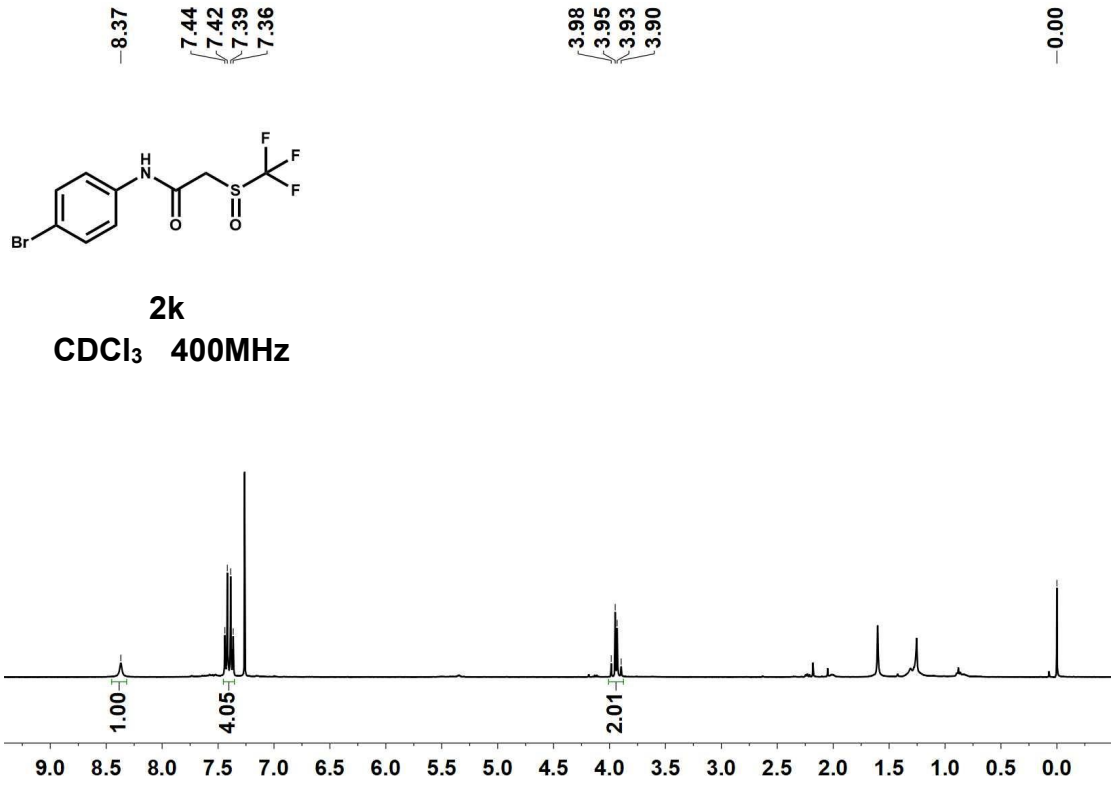
2i
$CDCl_3$ 376MHz



2j
$CDCl_3$ 400MHz

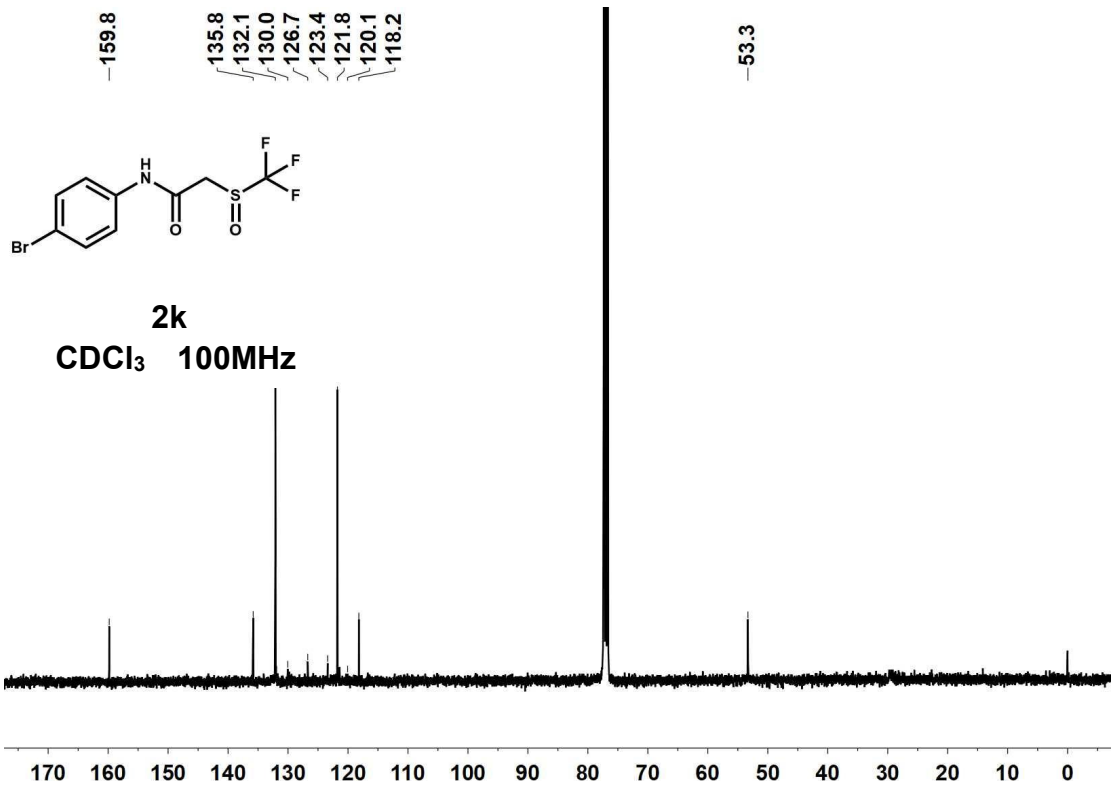

159.8
135.3
130.5
130.1
129.1
126.7
123.4
121.4
120.1
53.7
2j
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


71.86
2j
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



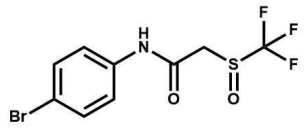
2k

$CDCl_3$ 400MHz



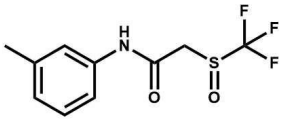
2k

$CDCl_3$ 100MHz



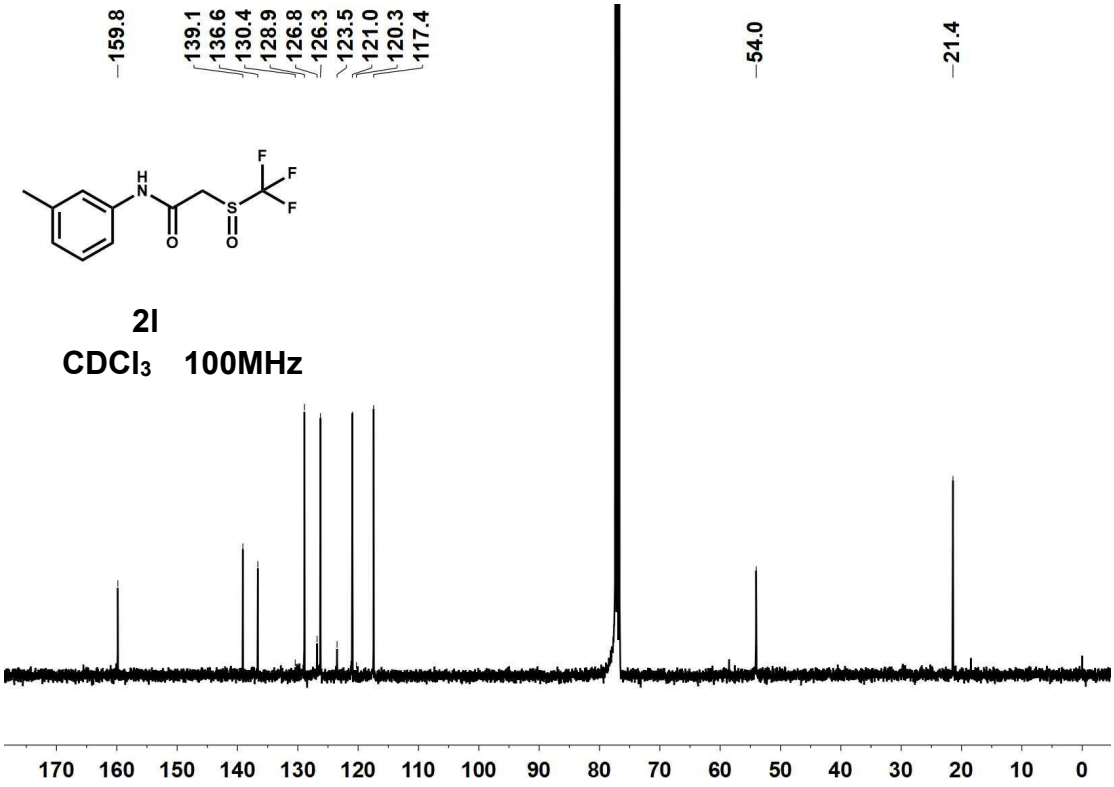
2k

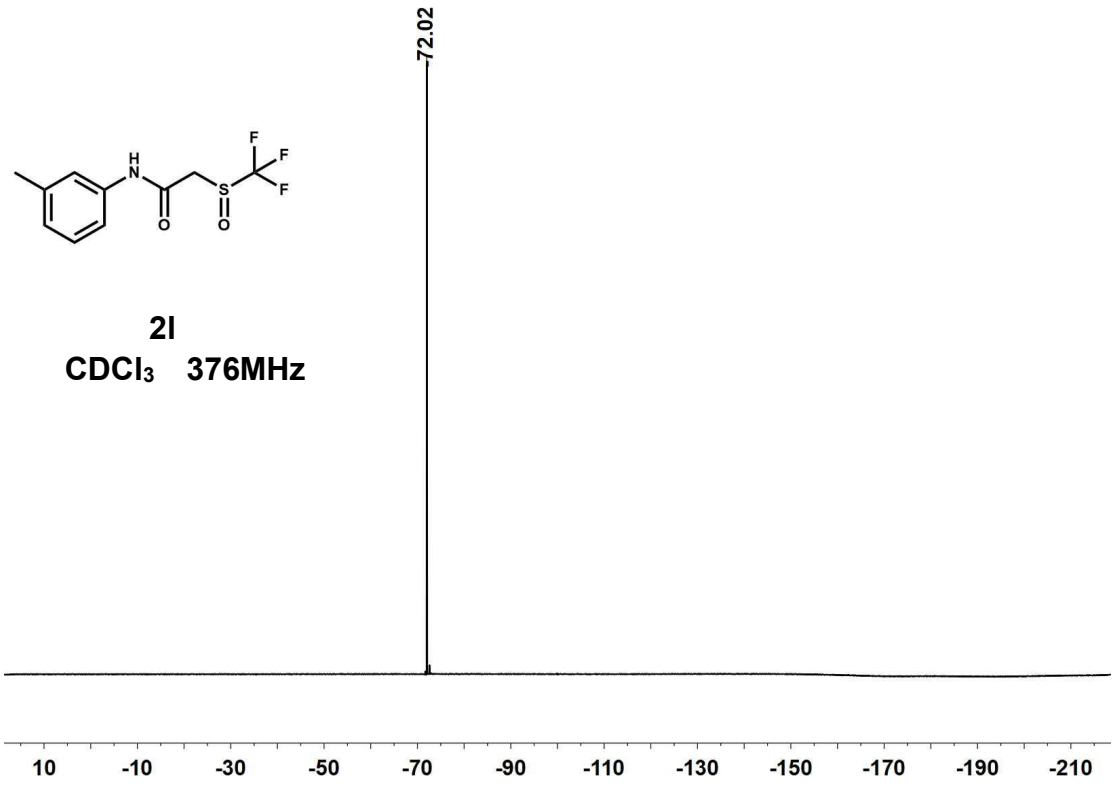
$CDCl_3$ 376MHz

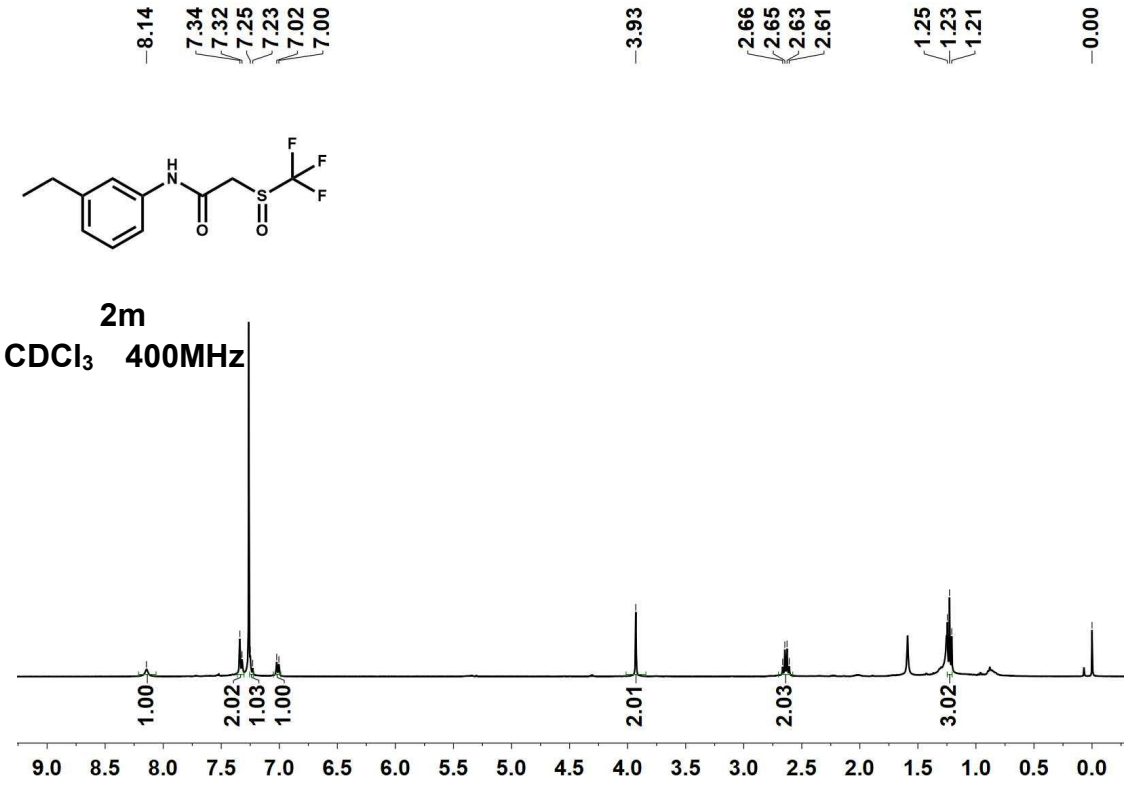


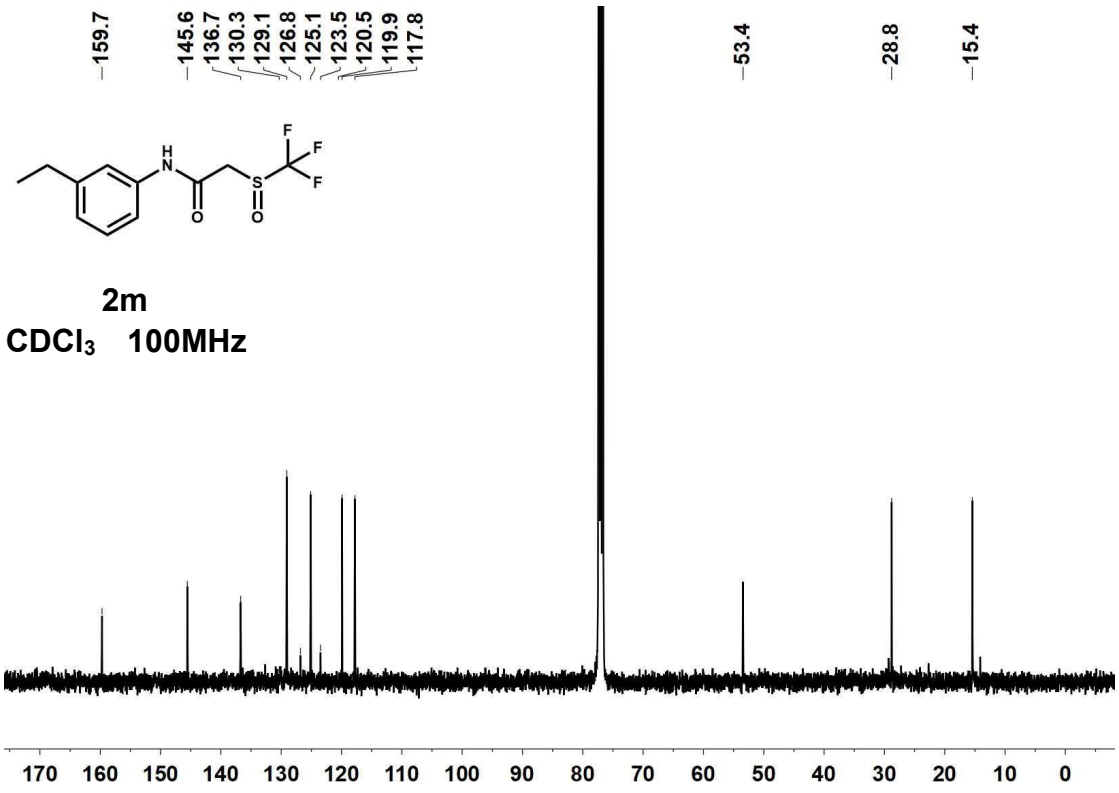
2l

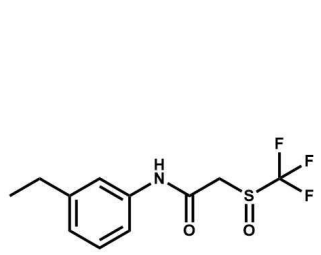
$CDCl_3$ 400MHz


159.8
139.1
136.6
130.4
128.9
126.8
126.3
123.5
121.0
120.3
117.4
54.0
21.4
H
N
O
S
O
F
F
F
2l
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


72.02
H
N
O
S
O
F
F
F
2l
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

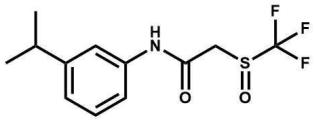

8.14
7.34
7.32
7.25
7.23
7.02
7.00
3.93
2.66
2.65
2.63
2.61
1.25
1.23
1.21
0.00
F
F
F
H
N
S
O
O
2m
CDCl3 400MHz
1.00
2.02
1.03
1.00
2.01
2.03
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


159.7
145.6
136.7
130.3
129.1
126.8
125.1
123.5
120.5
119.9
117.8
53.4
28.8
15.4
F
F
F
H
N
S
O
O
2m
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



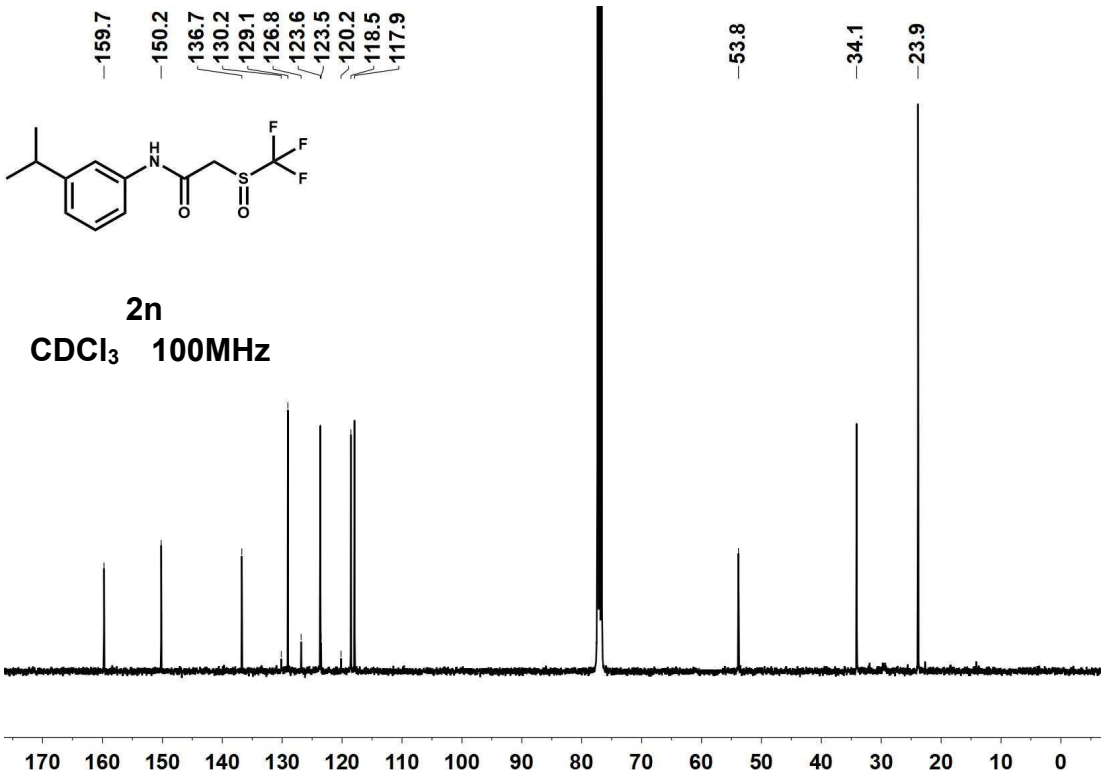
2m

$CDCl_3$ 376MHz



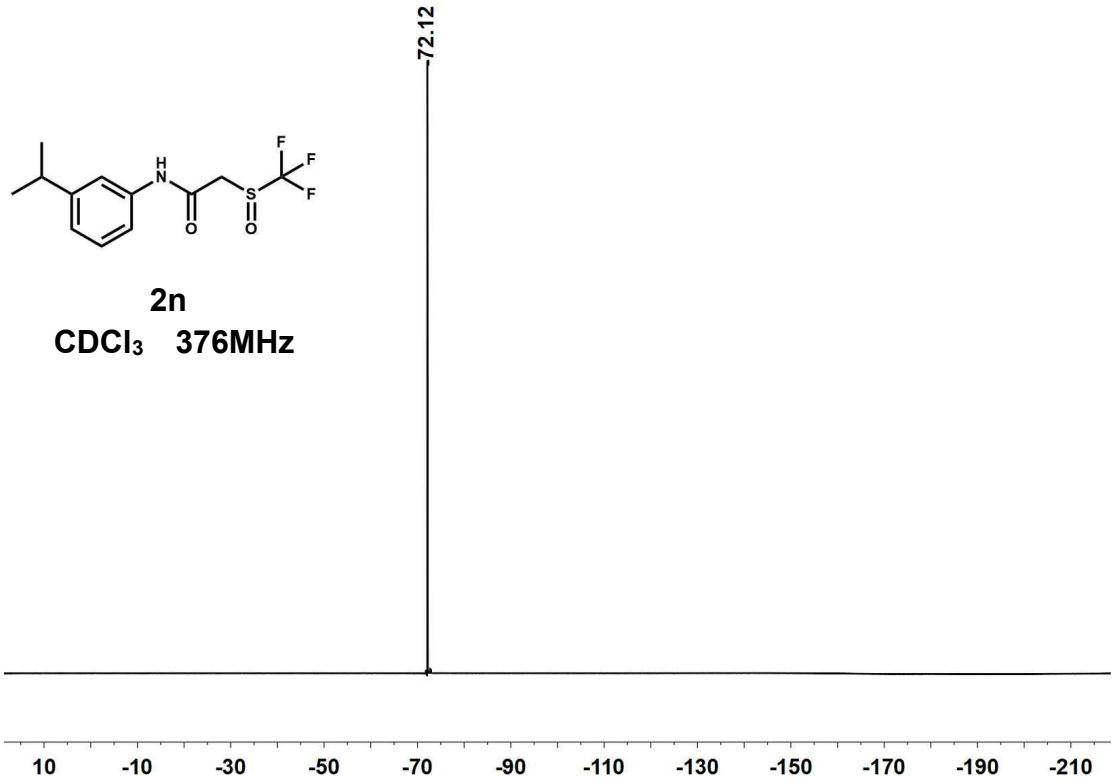
2n

$CDCl_3$ 400MHz



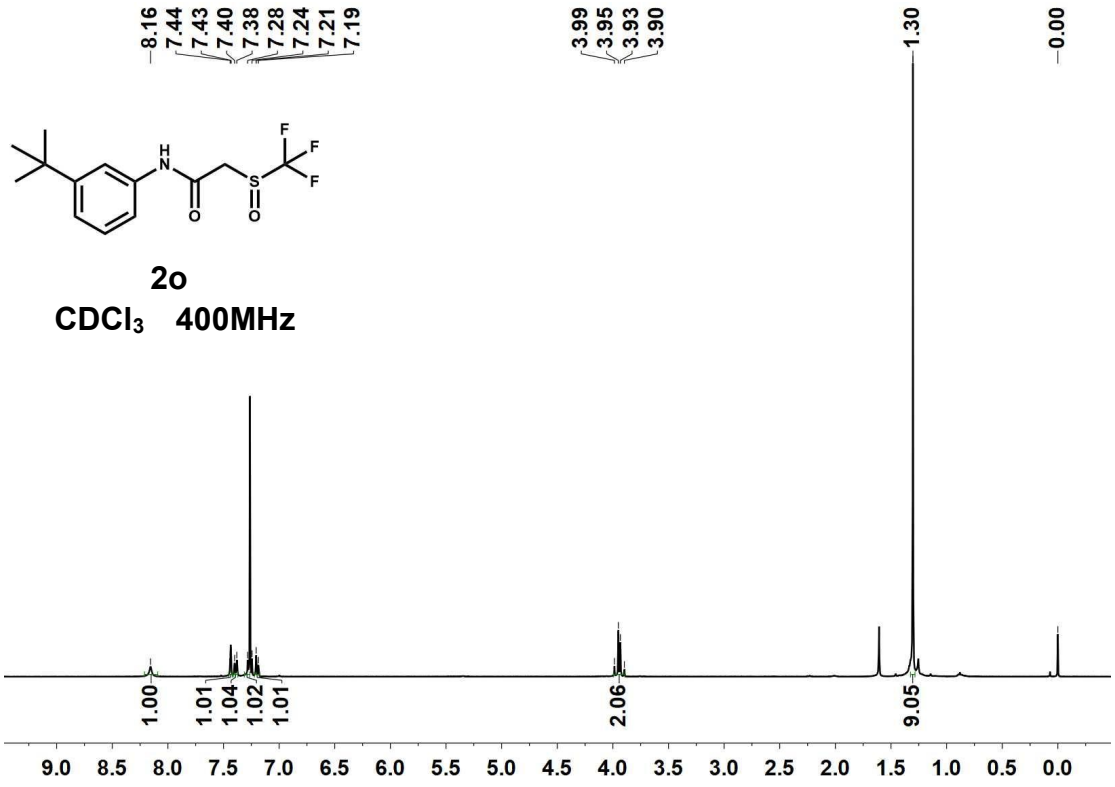
2n

$CDCl_3$ 100MHz



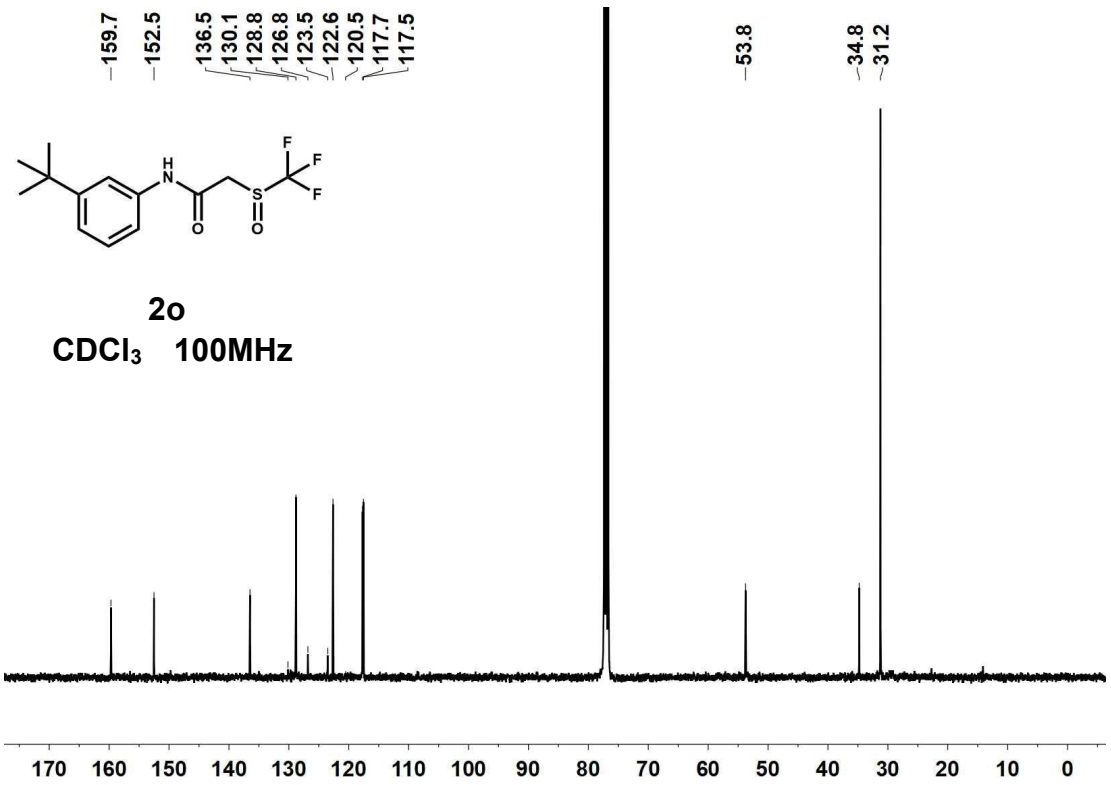
2n

$CDCl_3$ 376MHz



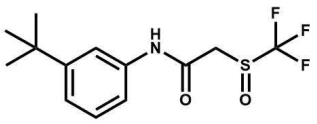
2o

$CDCl_3$ 400MHz



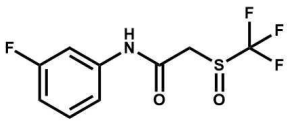
2o

$CDCl_3$ 100MHz



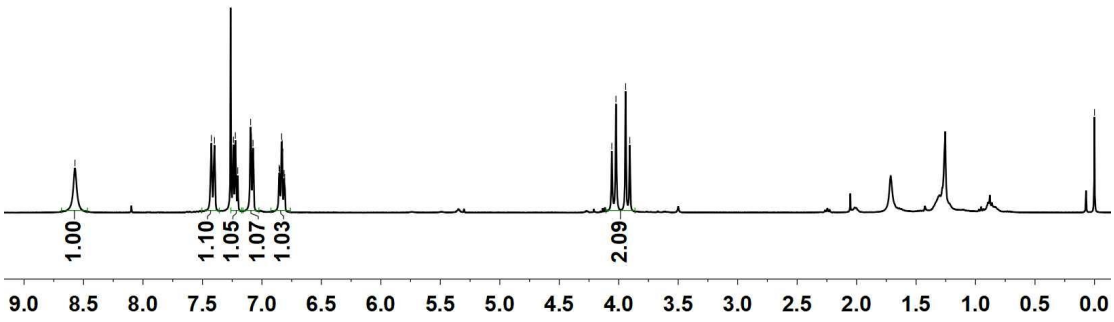
2o

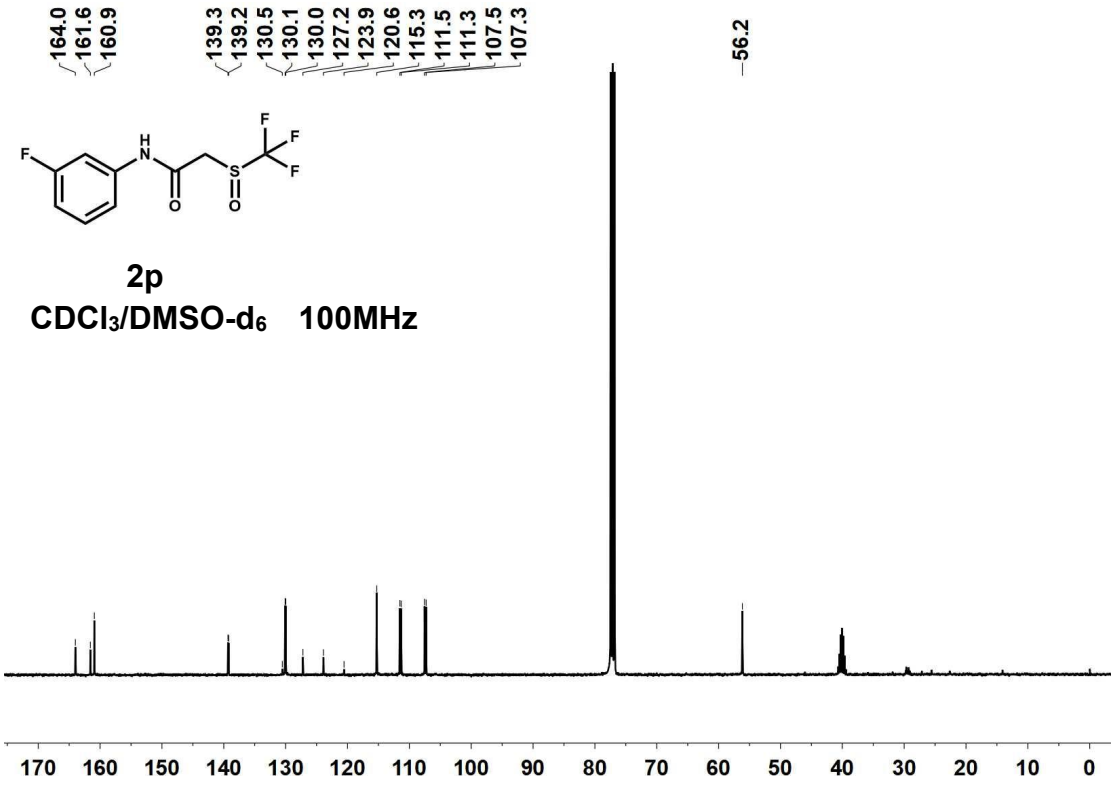
$CDCl_3$ 376MHz



2p

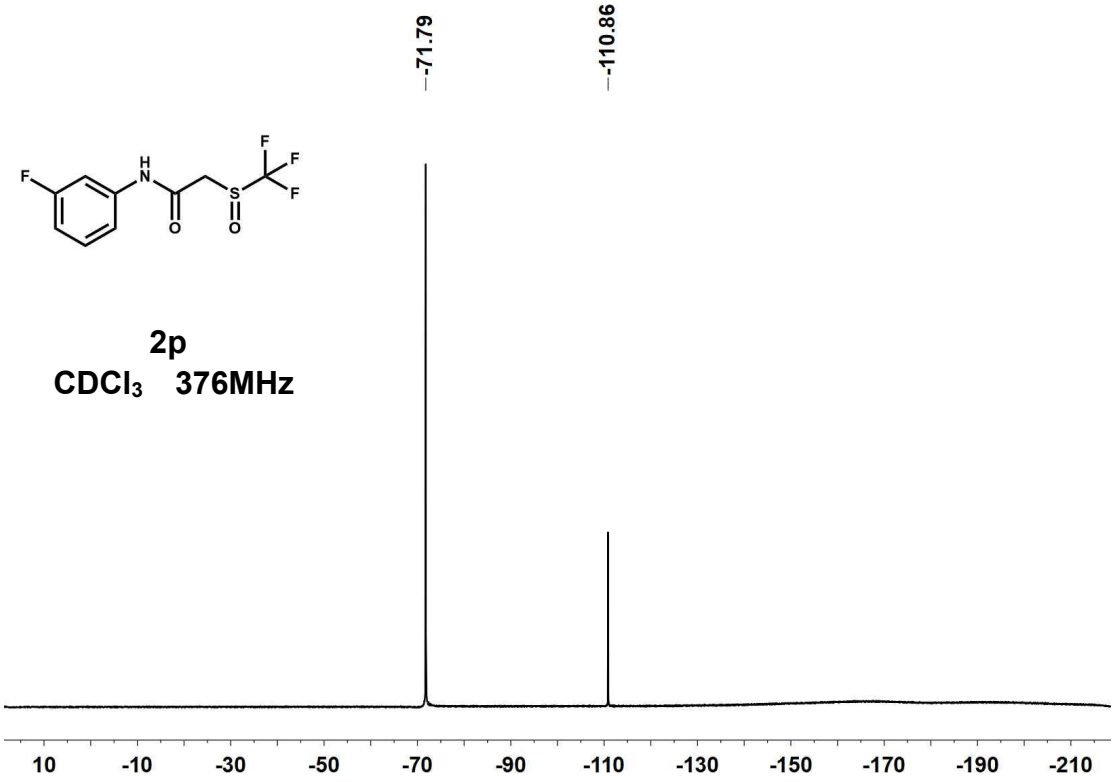
$CDCl_3$ 400MHz





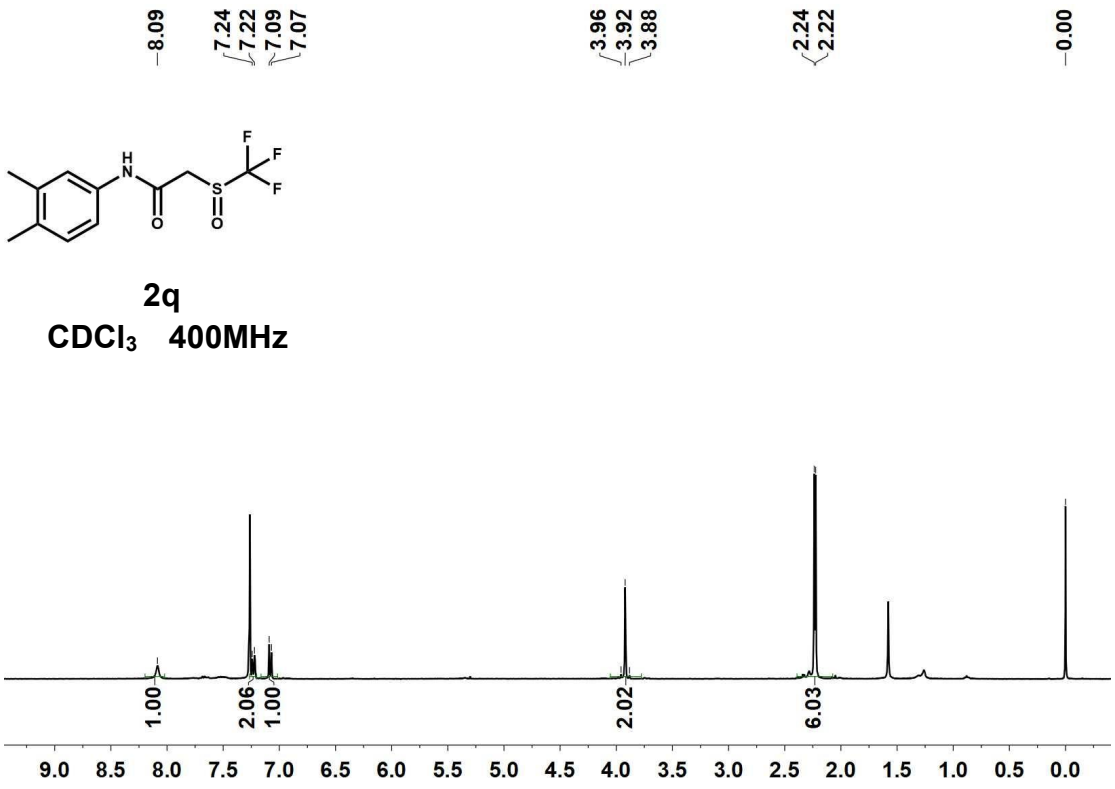
2p

$CDCl_3$/DMSO-d_6 100MHz



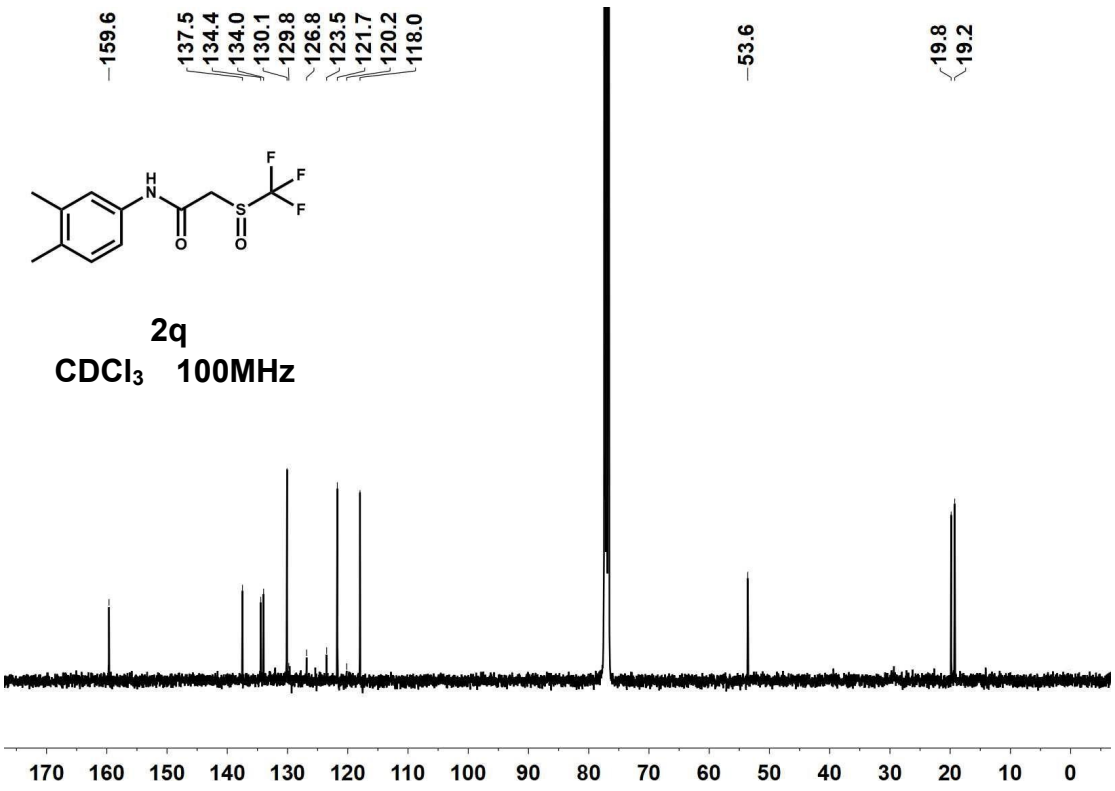
2p

$CDCl_3$ 376MHz



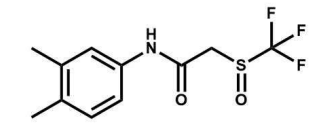
2q

$CDCl_3$ 400MHz



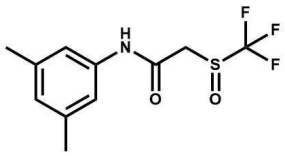
2q

$CDCl_3$ 100MHz



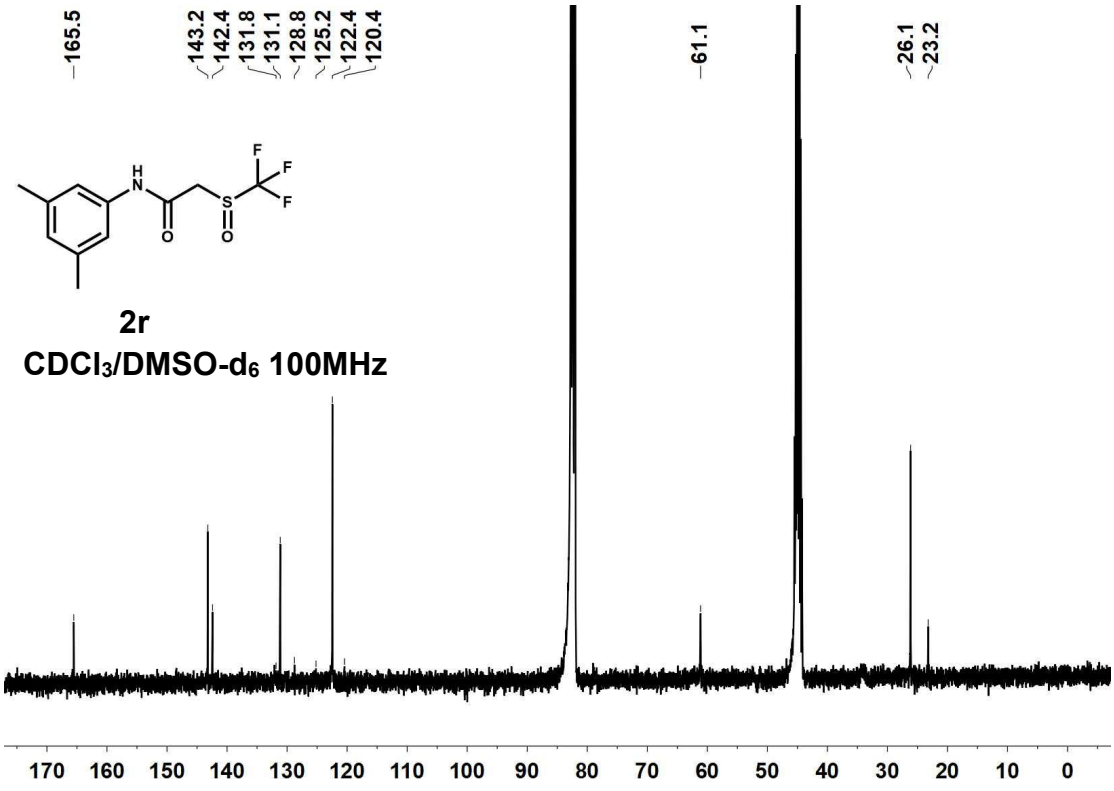
2q

$CDCl_3$ 376MHz



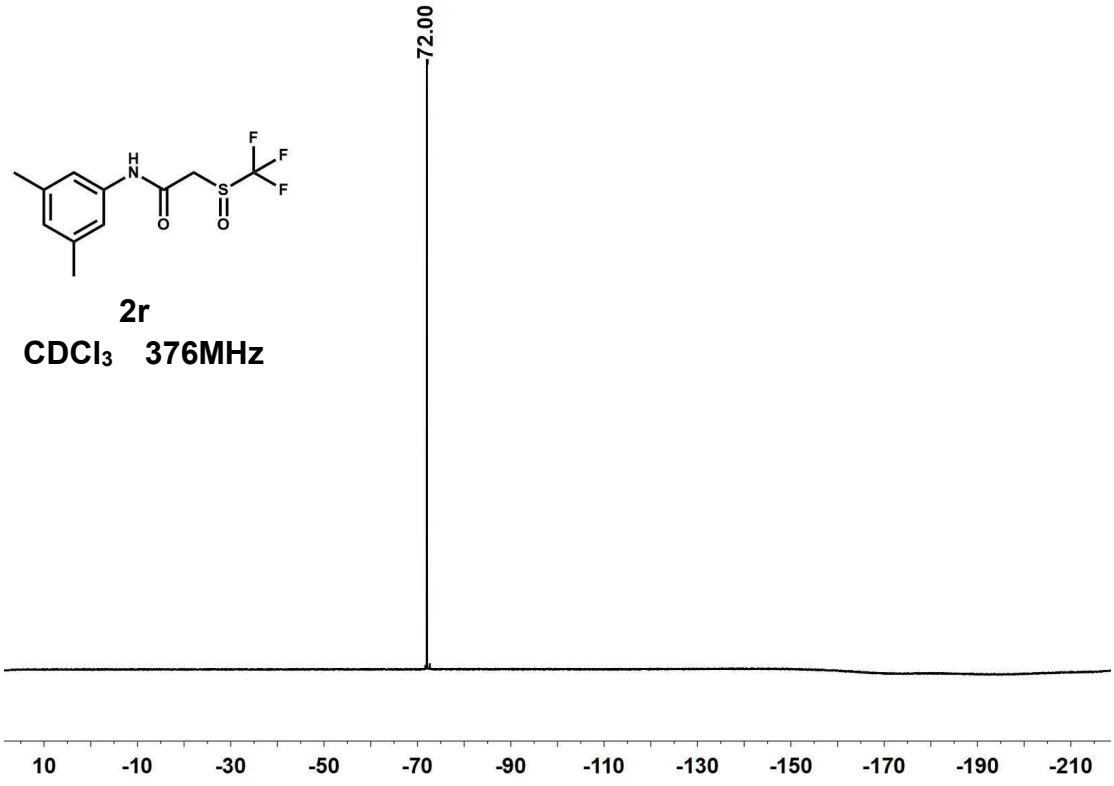
2r

$CDCl_3$ 400MHz



2r

$CDCl_3$/DMSO-d_6 100MHz



2r

$CDCl_3$ 376MHz